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HYDROPROCESSING OF HEAVY GAS OIL IN A CONTINUOUS STIRRED TANK REACTOR

by

© GREGORY P. MAN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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ABSTRACT

A conventional 0.3 L high pressure autoclave was converted into a small scale continuous flow stirred tank reactor (CSTR) system. The reactor system was used to study the hydroprocessing of heavy gas oil derived from thermally hydrocracked Athabasca bitumen. Advanced analytical techniques, including gas chromatography for simulation of boiling point distribution analysis and X-ray fluorescence for determination of sulfur content, were employed to analyze the hydrocarbon products.

The study of thermal hydroprocessing covered a liquid hourly space velocity range of 1.0 to 5.0 h^{-1} and a hydrogen to oil ratio range of 200 to 600 m^3API/m^3. Two levels of pressure (13.8 and 17.2 MPa) and one temperature (450°C) were examined.

A reasonable fit of experimental data was obtained by assuming first order and second order rate expressions, respectively, for the thermal hydrocracking and thermal hydrodesulfurization of heavy gas oil.

It was also observed that at constant temperature and pressure, the extent of thermal hydrocracking and hydrodesulfurization, together with the hydrogen consumption, increased as the liquid hourly space velocity decreased. In addition, at the same temperature, the hydrogen consumption increased and the hydrocarbon gas make decreased, with increasing reaction pressure.

This study has demonstrated that a small scale stirred tank reactor system offers a viable alternative to a tubular reactor for the study of thermal hydroprocessing of hydrocarbon feedstocks. It should be particularly useful in obtaining kinetic data that are free of interference from mass transport effect and mixing pattern.

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NOMENCLATURE

a	correlation constant
A	agitator speed
b	correlation constant
B	correlation constant
C	weight %, concentration
CA	chromatographic area
d	time delay
D	correlation constant
E	correlation constant
F	liquid volumetric flow rate
G	cumulated volume
G	volumetric flow rate
H	hydrogen consumption
HAGO	heavy atmospheric gas oil
HC	hydrocracking
HDM	hydrodemetallization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HGO	heavy gas oil
k	rate constant
K	adsorption equilibrium constant
LH	liquid holdup
LHSV	liquid hourly space velocity
M	cumulated weight

$\dot{M}$	mass flow rate
MW	molecular weight
n	reaction order
P	reaction pressure
P'	partial pressure
r	rate of reaction
R	gas constant
RGA	refinery gas analysis
RTD	residence time distribution
S	difference between theoretical and measured values
SDA	simulated distillation analysis
SG	specific gravity
t	time, residence time, reaction time
T	reaction temperature
TBP	true boiling point
V	volume %, volume
VP	vapour pressure
W	weight
x	mole fraction
X	fractional conversion
α	fraction
Δ	change
ε	discrepancy in mass balance
τ	contact time

Subscripts

C_i	hydrocarbon with carbon number of i
C_7	n-heptane
D	distillate
f	feed
F	fuel oil
g	gas
H_2	hydrogen
H_2S	hydrogen sulfide
HAGO	heavy atmospheric gas oil
HC	hydrocracking
HDN	hydrodenitrogenation
HDS	hydrodesulfurization
i	reactor inlet
l	liquid
m	measured value
N	naphtha
NH_3	ammonia
o	reactor outlet
p	product
P'_H	partial pressure of hydrogen
P'_O	partial pressure of oil
S	sulfur, sulfur compound
S_1	reactive sulfur compound
S_2	less reactive sulfur compound

STP	standard temperature (15°C) and standard pressure (101.3 MPa)
T	reaction temperature
∞	infinity

I. INTRODUCTION

Both thermal and catalytic hydroprocessing have important roles to play in the efficient upgrading of unconventional hydrocarbon energy resources. This is particularly true in the upgrading of bitumen and heavy oils where hydrogen-addition (hydrocracking), potentially, offers a higher liquid yield and reduces the coke disposal problem associated with the carbon-removal (coking) process.

Since the early 1960's the Canadian Centre for Mineral and Energy Technology (CANMET) has carried out extensive research work on developing an economical process (Thermal Hydrocracking) for upgrading bitumen and heavy oils. Their work was conducted using conventional tubular reactors. The application of tubular reactor to obtain intrinsic kinetic data suffers from the uncertainties regarding the internal flow patterns and whether mass transport significantly affects the observed reaction rate. It was felt that such disadvantages could be minimized by the use of a continuous flow stirred tank reactor.

In 1977, a research program was initiated in the Department of Chemical Engineering of the University of Alberta, to complement CANMET's research work in the area of hydrocracking. This report describes a part of this research program.

The main objective of this work is to demonstrate the usefulness of a small scale continuous flow stirred tank

reactor system for the kinetic study of hydroprocessing of hydrocarbon feedstock. The intrinsic rate data and product distribution obtained can be used for reactor sizing purposes. The secondary objective is to examine the thermal hydrocracking of heavy gas oil derived from thermally hydrocracked Athabasca bitumen. The final, but not the least important, objective is to establish the necessary analytical techniques and facilities that are pertinent to the successful application of this type of small scale reactor.

II. LITERATURE SURVEY

Hydroprocessing plays a significant role in the upgrading of hydrocarbon resources like coal, bitumen, crude oil and shale oil by increasing the hydrogen to carbon ratio in such fuels. It is used to produce lighter and cleaner liquid products from these heavier feedstocks and is considered to be the most versatile process in the petroleum refining industry.

It includes processes such as hydrocracking (HC), hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodemetallization (HDM).

Based on the severity of the reaction, hydroprocessing can be divided into two main categories:

Hydrogenolysis and Hydrocracking

This group of hydroprocessing reactions generally occur at high pressure (10.3-17.2 MPa) and high temperature (370-480°C). When the reaction involves bond cleavage, it is called hydrogenolysis. When the hydrogenolysis reaction entails complete cleavage of carbon-carbon bonds, it is described as hydrocracking.

Hydrotreating

Hydrotreating reactions tend to occur at comparatively lower pressure (3.4-6.9 MPa) and lower temperature (260-370°C). They include reactions such as HDS, HDN and HDO

which involve the breaking of carbon-sulfur, carbon-nitrogen and carbon-oxygen bonds, and hydrogenation where hydrogen is added to unsaturated compounds.

It is important to recognize that when hydrogen is allowed to react with petroleum products, all the above mentioned reactions will occur to a certain degree. The extent of each reaction will depend on its relative reaction rate.

Numerous commercial catalysts have been developed over the years which are used to enhance certain desirable hydroprocessing reactions and suppress others. They may be very selective. For example, cobalt-molybdate on alumina is commonly used for HDS reactions, while nickel-molybdate on alumina is recommended for HDN reactions. Current emphasis in this area is on developing hydrocracking catalysts that are more selective and less prone to deactivation.

Since the literature information on hydroprocessing reactions is extensive, the following survey will be confined to: (1) hydrocracking and hydrodesulfurization in relationship to the processing of petroleum feedstocks and, (2) the development of fundamental information required for the design of operations used for the hydroprocessing of petroleum feedstocks.

A. Hydrocracking

Hydrocracking has gained widespread acceptance in the last 20 years. Recent interest in hydrocracking, however, lies predominantly in converting residue and other unconventional sources of hydrocarbon (such as coal, shale oil and bitumen) into lighter and cleaner fuels. Basically, hydrocracking can be carried out in two ways: thermally or catalytically.

Thermal Hydrocracking

The Energy Research Laboratories of CANMET[1] have expended considerable effort in developing a thermal hydrocracking process for producing light liquid product from heavy residue like Athabasca bitumen. Thermal hydrocracking is seldom considered, under normal refinery conditions, because to hydrocrack deeply into the residue fraction, abnormally high pressure and temperature are required and hence, high capital investment. In addition, there has been a phenomenal growth in the understanding of the function of hydrocracking catalysts and their demonstrated ability to produce products that are in high demand like gasoline from petroleum feedstocks with low metal content and less tendency to form coke. The main incentive for applying thermal hydrocracking to bitumen is the elimination of operating problems associated with catalyst fouling due to coking and metal contamination.

---

[1] Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Ottawa.

However, similar incentive does not apply to lighter feedstocks such as gas oils derived from unconventional hydrocarbon resources, which explains why there is little published work on thermal hydrocracking of gas oils derived from Athabasca bitumen.

Since 1960, researchers in the Energy Research Laboratories of CANMET have studied different aspects of thermal hydrocracking of Athabasca bitumen. Their experiments were conducted in conventional tubular reactors with internal diameters ranging from 2.5 to 3.8 cm, and lengths ranging from 0.3 to 4.0 m. Both the bitumen and hydrogen were fed into the reactor from the bottom. Reactor effluents entered a hot receiver where vapor product was separated from liquid product. The liquid product was transferred to a heavy oil tank which was maintained at atmospheric pressure and the vapor product was condensed and collected in a cold receiver. The condensed liquid was allowed to enter a low pressure light oil tank, while the uncondensed vapor was recycled back to the reactor after being oil-scrubbed.

In 1969, Cameron and co-workers (3) compared thermal with catalytic hydrocracking of Athabasca bitumen. They showed that at high pressure, thermal hydrocracking resulted in lower liquid yield than catalytic hydrocracking. Furthermore, thermal hydrocracking was found to be capable of removing 25 to 26% of the sulfur in the feed, as compared with 73% to 75% by catalytic hydrocracking.

In 1973 Merrill and co-workers (15) reported their work on thermal hydrocracking of Athabasca bitumen. They found that the sulfur removal and the pitch (524°C + fraction) conversion increased with increasing pressure. On the other hand, hydrogen consumption increased and hydrocarbon off gas decreased with increasing pressure. In addition, they demonstrated that at the same pressure, an increase in temperature resulted in an increase of sulfur removal, pitch conversion, hydrogen consumption and hydrocarbon gas make.

Khulbe and co-workers (12) reported their operational experience of a thermal hydrocracking pilot plant, when heavy oil was recycled. They found that heavy oil recycling had the following effects:

1. Smoother operation
2. Reduced coke formation in the reactor
3. Increased hydrogen consumption
4. Decreased pitch conversion
5. Decreased total liquid product
6. Increased nitrogen removal

Catalytic Hydrocracking

Literature information on catalytic hydrocracking is extensive and covers a wide range of feedstocks (n-hexane to heavy bitumen). The reactor used in the study of catalytic hydrocracking is predominantly a trickle bed type of reactor. In the analysis of data obtained from trickle bed reactors, it is necessary to segregate the hydrodynamic effects (such as holdup, incomplete catalyst wetting and

backmixing) and the various mass transfer resistances, in order to obtain the intrinsic reaction rate.

In 1969, Qader and Hill (18) reported their work on hydrocracking of gas oil. They hydrocracked a gas oil with a boiling range of 300-400°C in a continuous fixed bed tubular reactor over a dual-function catalyst (nickel-tungsten sulfides on silica-alumina support). The reactor had an internal diameter of 1.91 cm and was 1.02 m long. The results suggested that the hydrocracking of gas oil involves both simultaneous and consecutive bond-breaking reactions which are followed by isomerization and hydrogenation. In addition, by treating the gas oil, sulfur and nitrogen compounds as single components, they found the overall reaction rates of HC, HDS and HDN to be each first order. The rate constants obtained by assuming the reactor used was a plug flow type of reactor were

$$k_{HC} = 1 \times 10^{7} \exp\left(-\frac{21100}{RT}\right) \qquad (2.1)$$

$$k_{HDS} = 0.6814 \times 10^{5} \exp\left(-\frac{16800}{RT}\right) \qquad (2.2)$$

$$k_{HDN} = 0.8253 \times 10^{5} \exp\left(-\frac{17400}{RT}\right) \qquad (2.3)$$

where k_{HC}, k_{HDS}, k_{HDN} = rate constants for hydrocracking, hydrodesulfurization and hydrodenitrogenation respectively, h^{-1}

R = gas constant

T = reaction temperature, K

Paraskos and co-workers (17) studied the effects of liquid holdup, incomplete catalyst wetting and backmixing on kinetic data obtained from a bench scale trickle bed reactor. The reactor was 2.54 cm in diameter and 1.12 m long. The feedstock they used included a 53% reduced Kuwait crude, a 50-50 blend by volume of Kuwait and California furnace oils, a Kuwait vacuum gas oil and a Kuwait light gas oil. Using the "effective catalyst wetting" model proposed by Mears (14) and the holdup model proposed by Henry and Gilbert (9), they showed HDS, HDN and HDM to be of first order.

Aitken, Merrill and Pleet (1) studied the hydrogenation of a coker distillate over a fixed bed of cobalt molybdate on alumina catalyst (3.81 cm outside diameter and 76.2 cm long). The coker distillate was derived from Athabasca bitumen.

They related the effect of reaction pressure and running time to the product specific gravity, at 480°C and an hourly space velocity of 2.0, by the following empirical expression:

$$\frac{\Delta SG}{\Delta t} = \frac{1.24 \times 10^{4}}{P^{3.1}} \qquad (2.4)$$

where ΔSG = change in product specific gravity

Δt = increment of running time, h

P = reaction pressure, psi

They also found that the product weight yield increased with increasing pressure, due to the suppression of gas oil cracking to form gaseous hydrocarbons. In addition, the removal of sulfur and nitrogen was found to be enhanced by increased pressure. At constant pressure and temperature, a decrease of space velocity resulted in an increase in the extent of hydrocracking, and of sulfur and nitrogen removal.

B. Hydrodesulfurization

There is a recent surge in interest on the subject of hydrodesulfurization. This is motivated by an increasing demand for low sulfur fuel oils and more stringent pollution control standards. The literature on the chemistry and technology of HDS has been reviewed by McKinley (13), Schuman and Shalit (21), and more recently by Schuit and Gates (20).

In 1950, Hoog (11) studied the effect of molecular weight of petroleum fractions on the rate of hydrodesulfurization. The feedstock used was a Middle East gas oil with a boiling range of 260 to 350°C, and two narrow boiling point fraction derived from this gas oil (290 to 300°C, and 330 to 340°C). The catalyst employed was cobalt molybdate on alumina support. His results showed that the rate of HDS for the lighter fraction was faster than that for the heavier fraction. He attributed this to the steric effect of the different kinds of sulfur compounds in each fraction. In addition, he showed that the HDS of the narrow

fractions was a first order reaction.

$$\ln \left(\frac{P'_{s,o}}{P'_{s,i}}\right) = -k_{HDS}\,\tau \qquad (2.5)$$

where $P'_{s,i}$ = partial pressure of sulfur compounds at the inlet of the reactor bed

$P'_{s,o}$ = partial pressure of sulfur compounds at the outlet of the reactor bed

k_{HDS} = rate constant at a given hydrogen partial pressure and temperature

τ = apparent contact time

$\frac{P'_{s,o}}{P'_{s,i}}$ = ratio of final and initial sulfur concentration in the oil

$$= \frac{C_{s,o}}{C_{s,i}}$$

Beuther and Schmid (2) did an extensive study on the catalytic HDS of high sulfur Middle East reduced crudes. The catalyst used was not specified. The study covered a wide range of operating conditions: a temperature range of 365 to 450°C, a liquid hourly space velocity range of 0.5 to 5 h^{-1}, and a pressure range of 1.7 to 20.7 MPa. They found that the rate of HDS could be represented by a simple second order equation

$$r_{HDS} = -k\,C_s^2 \qquad (2.6)$$

where r_{HDS} = rate of HDS, h^{-1}

k = reaction rate constant, h^{-1}

C_s = weight % of sulfur

The activation energy for the second order reaction was determined to be 59 kJ/mole. Furthermore, they showed that the effect of pressure on the reaction rate constant was substantial between 1.7 to 13.8 MPa. At higher pressure, the effect became less significant.

Frye and Mosby (6) examined the HDS of individual sulfur compounds in light cycle oils. The oils contained 0.4 to 2.0 weight percentage of sulfur. The catalyst used was cobalt-molybdate on alumina. Detailed sulfur analyses of liquid samples were carried out by means of gas chromatography using a detector that was sensitive to sulfur compounds only. Three of the sulfur compounds identified, two in the trimethylbenzothiophene boiling range and the third in the dibenzothiophene range, were studied in detail. They found that HDS of individual sulfur compounds could be represented by a first order equation

$$r_{HDS} = k_{HDS} P'_S P'_H \qquad (2.7)$$

where r_{HDS} = rate of HDS of a single sulfur compound

k_{HDS} = rate constant

P'_S, P'_H = partial pressures of the sulfur compound and hydrogen respectively

Partial pressure of the sulfur compound, P'_S, was determined by assuming Raoult's law to be applicable

$$P'_S = x\ VP_S \tag{2.8}$$

where VP_S, P'_S = vapor pressure and partial pressure of a single sulfur compound

x = mole fraction of the sulfur compound

Their results also confirmed that the lower boiling sulfur compounds were easier to desulfurize than the higher boiling sulfur compounds.

In a 1973 review, Schuit and Gates (20) suggested that the sulfur compounds in the feed could be considered to be made up of two hypothetical sulfur-containing components, one reactive and the other less reactive. The desulfurization of each component was assumed to be a first order reaction

$$r_{HDS} = -\ (k_{S_1} \alpha_{S_1} C_S + k_{S_2} \alpha_{S_2} C_S) \tag{2.9}$$

where r_{HDS} = reaction rate of HDS

α_{S_1} = fraction of sulfur compound that is reactive

α_{S_2} = fraction of sulfur compound that is less reactive, $1 - \alpha_{S_1}$

C_S = weight % of sulfur compound

At practical HDS conditions, the more reactive fraction of sulfur compound, $\alpha_{S_1} C_{S_1}$, rapidly depleted to zero so that the second term, $k_{S_2} \alpha_{S_2} C_S$, became controlling.

They also proposed the following equation for high conversion HDS equation

$$r_{HDS} = \frac{k_{S_2}\alpha_{S_2}C_S P'_{H_2S}}{1 + K_{H_2}P'_{H_2} + K_{H_2S}P'_{H_2S}} \qquad (2.10)$$

where K_{H_2}, K_{H_2S} = adsorption equilibrium constants for hydrogen and hydrogen sulfide respectively

P'_{H_2}, P'_{H_2S} = partial pressures for hydrogen and hydrogen sulfide respectively.

In 1973, Soutar and co-workers (22) investigated the hydrodesulfurization of three gas oils derived from Athabasca bitumen. One of the gas oils was obtained commercially, using delayed coking and had a boiling range of 260 to 450°C. The other two were obtained from pilot plants using thermal and catalytic hydrocracking respectively.

The reactor used was a fixed bed (3.18 cm in diameter) of commercial cobalt molybdate on alumina catalyst. An upflow system was employed, where both the liquid feedstock and the hydrogen percolated up through the reactor. This was different from the more extensively used downflow trickle bed reactor. The study covered a temperature range of 320 to 420°C, and a liquid hourly space velocity range of 1 to 3 h^{-1}. The hydrogen flow rate used was 890 m^3/m^3.

They found the reaction characteristics of the three gas oils were very similar. An increase of reaction temperature resulted in a decrease in sulfur content and in specific gravity of the liquid product. No kinetic data were presented in the study.

In a study of hydrodesulfurization of residual fuel oils, Ozaki et al. (16) showed that the apparent reaction order of desulfurization varied with temperature. A packed bed of nickel, cobalt and molybdenum oxides supported on alumina was used. The reactor was 25 mm in diameter and 1.20 m in length. The operating conditions examined covered a temperature range of 320 to 440°C, and a liquid hourly space velocity of 0.5 to 3.0 h^{-1} at a pressure of 11.8 MPa.

They demonstrated that the hydrodesulfurization of residual fuel oil followed a n-th order reaction,

$$r_{HDS} = -k_T \, X_S^{\,n} \qquad (2.11)$$

where r_{HDS} = rate of hydrodesulfurization, h^{-1}

k_T = reaction rate constant at temperature T(°C), h^{-1}

n = apparent reaction order

X_S = fractional conversion of sulfur

$$= 1 - \frac{\text{weight \% of sulfur in product}}{\text{weight \% of sulfur in feed}}$$

The apparent reaction rate constant, k_T, and the apparent reaction order, n, were related to the reaction temperature, T, by,

$$\log(k_T) = 2.349 - 0.04341 \exp(2447/T) \qquad (2.12)$$

$$n = 2388 \exp(-0.01067\ T) \qquad (2.13)$$

In addition, they also attempted to fit the result with a first order reaction by expressing the apparent rate constant, k_T, as a function of the residence time, t,

$$k_T = M\,[1 - B(\exp(D/t)] \qquad (2.14)$$

where t = residence time, h

M,B,D = correlation constants

Hisamitsu and co-workers (10) studied the hydrodesulfurization of two heavy distillates. The heavy distillates were vacuum gas oils obtained from different sources and had pronounced differences in physical properties. They used a conventional downflow tubular reactor. The reactor was 25 mm in diameter and 1.20 m long. One hundred milliliters of commercially available catalyst (cobalt and molybdenum oxides on alumina support) was used.

Like Ozaki et al., these investigators demonstrated that the apparent reaction order of hydrodesulfurization of vacuum gas oil varied with temperature. In fact, it decreased with an increase in reaction temperature (2.1 at 340°C, and 1.6 at 380°C). Furthermore, the results showed that the reaction rate order had a greater dependence on the boiling range of the liquid feed than on the other properties.

In 1976, Ranganathan and co-workers (19) compared the various competing reactions which occur simultaneously under severe hydroprocessing conditions. The feedstock they used

was a coker kerosene distillate (193 to 219°C) derived from Athabasca bitumen. They demonstrated that the desulfurization followed a second order reaction, while the denitrogenation followed a first order reaction. The results from the hydrogenation of aromatics, however, were found to fit neither first nor second order rate expressions.

In a 1977 study of the hydrodesulfurization of gas oil with a narrow boiling range (20°C), Yitzhaki and Aharoni (23) treated the overall desulfurization reaction as a sum of parallel and independent reactions. In addition, each individual reaction was assumed to be first order. The kinetics of the overall reactions were expressed by

$$C = \Sigma\, C_i \exp(-k_i t) \qquad (2.15)$$

where C = weight % of sulfur in product

C_i = weight % of individual sulfur compound, i, in feed

k_i = rate constant of sulfur compound, i, in feed, h^{-1}

t = reaction time, h

Furimsky (7) investigated the relative rate of catalytic removal of sulfur, nitrogen and oxygen from a heavy gas oil obtained from thermally hydrocracked Athabasca bitumen. The heavy gas oil had a boiling range of 345 to 525°C and was hydrotreated in a bench scale upflow fixed bed reactor with a volume of 155 cm^3 and a length to diameter ratio of 12. The catalysts used were mainly supported

molybdate with varying cobalt or nickel content. He concluded that the rate of HDS was the highest, followed by HDN and then HDO. In addition, he found that the difference between the promoting effects of nickel or cobalt in HDN and HDO of the heavy gas oil used was insignificant.

The literature survey shows that there is a general lack of information on the thermal hydroprocessing of light feedstocks derived from unconventional hydrocarbon resources which have high metal content and low hydrogen to carbon ratio. In addition, the predominant reactor used in the kinetic study of hydroprocessing is tubular reactor that suffers from the uncertainties regarding mixing pattern and mass transport effect. This work is an initial attempt to fill this gap by using a constant stirred tank reactor to study the hydroprocessing of a heavy gas oil derived from Athabasca bitumen.

III. REACTOR SYSTEM

A. Equipment

The hydroprocessing pilot unit constructed for this study consists of three basic sections: feed section, reaction section and separation section. Schematic diagrams of the unit are presented as Figures 1 and 2.

The main component of the unit is a high pressure autoclave. It has been modified and converted from a batch reactor to a continuous flow reactor.

The pilot unit is highly automated. It is designed to fulfil the anticipated need for extended runs of extended duration. Altogether five control loops have been implemented, so as to minimize the supervision required. In addition, all the controllers are electronic and can be interfaced with a computer for data logging purposes, if required. Detailed descriptions of the control loops can be found in Table 1.

Feed Section

The hydrogen gas used in the experiments was supplied by Linde Division of Union Carbide in 41.4 MPa commercial cylinders. Hydrogen pressure is reduced to 690 KPa above reactor pressure by a Matheson Model 3062B high pressure regulator, PRV-101.

The flow rate of the hydrogen feed to the reactor is controlled by measuring the pressure drop across a laminar

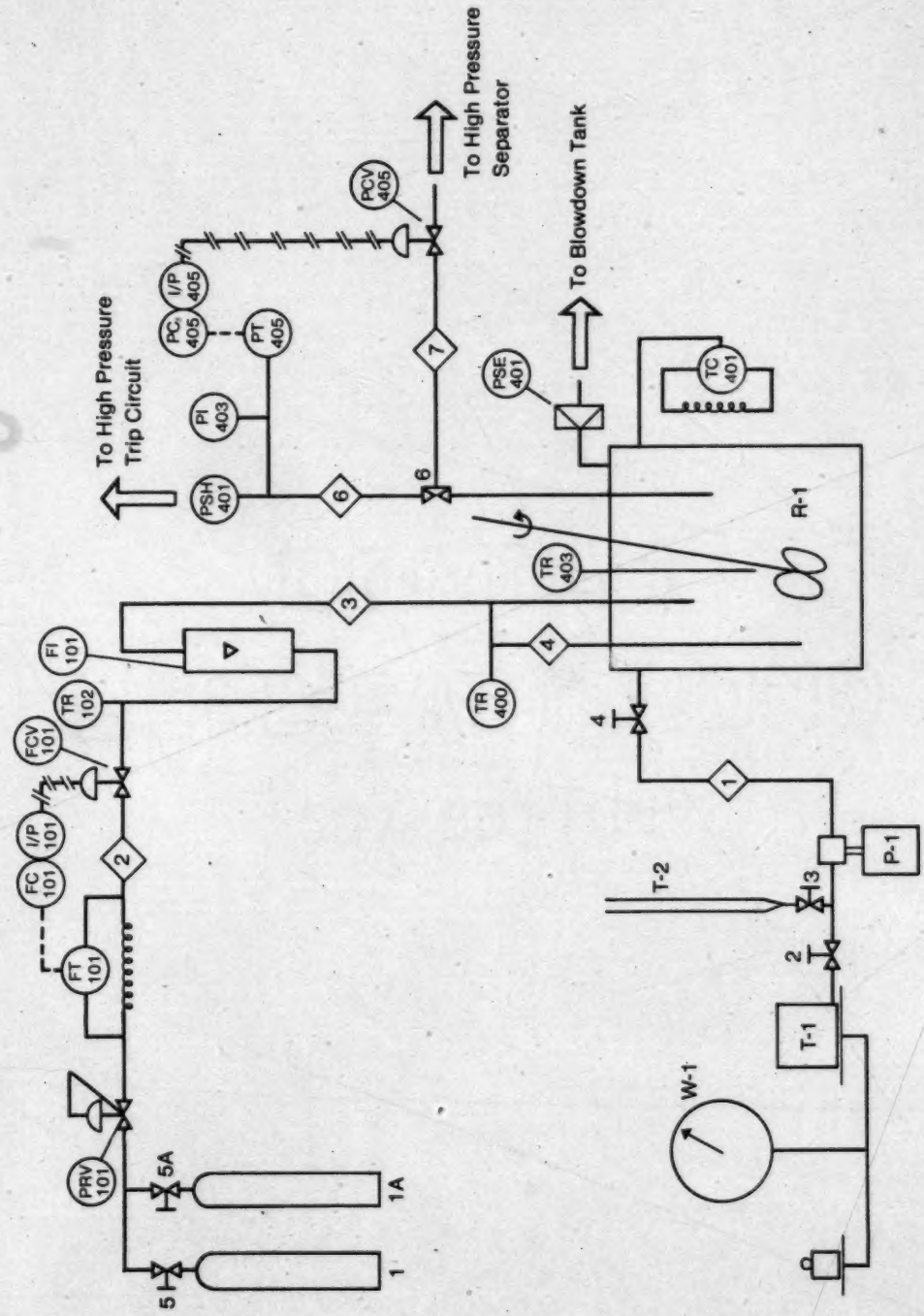


Figure 1: Feed and Reaction Section

Symbols for Figure 1

1	Hydrogen Cylinder
1A	Hydrogen Cylinder
2	Feed Tank Shutoff Valve
3	Burette Shutoff Valve
4	Shutoff Valve of Liquid Feed to Reactor
5	Cylinder Shutoff Valve
5A	Cylinder Shutoff Valve
6	Three-way Valve
P-1	Liquid Feed Pump
R-1	Reactor
T-1	Liquid Feed Pump
T-2	Burette
W-1	Scale

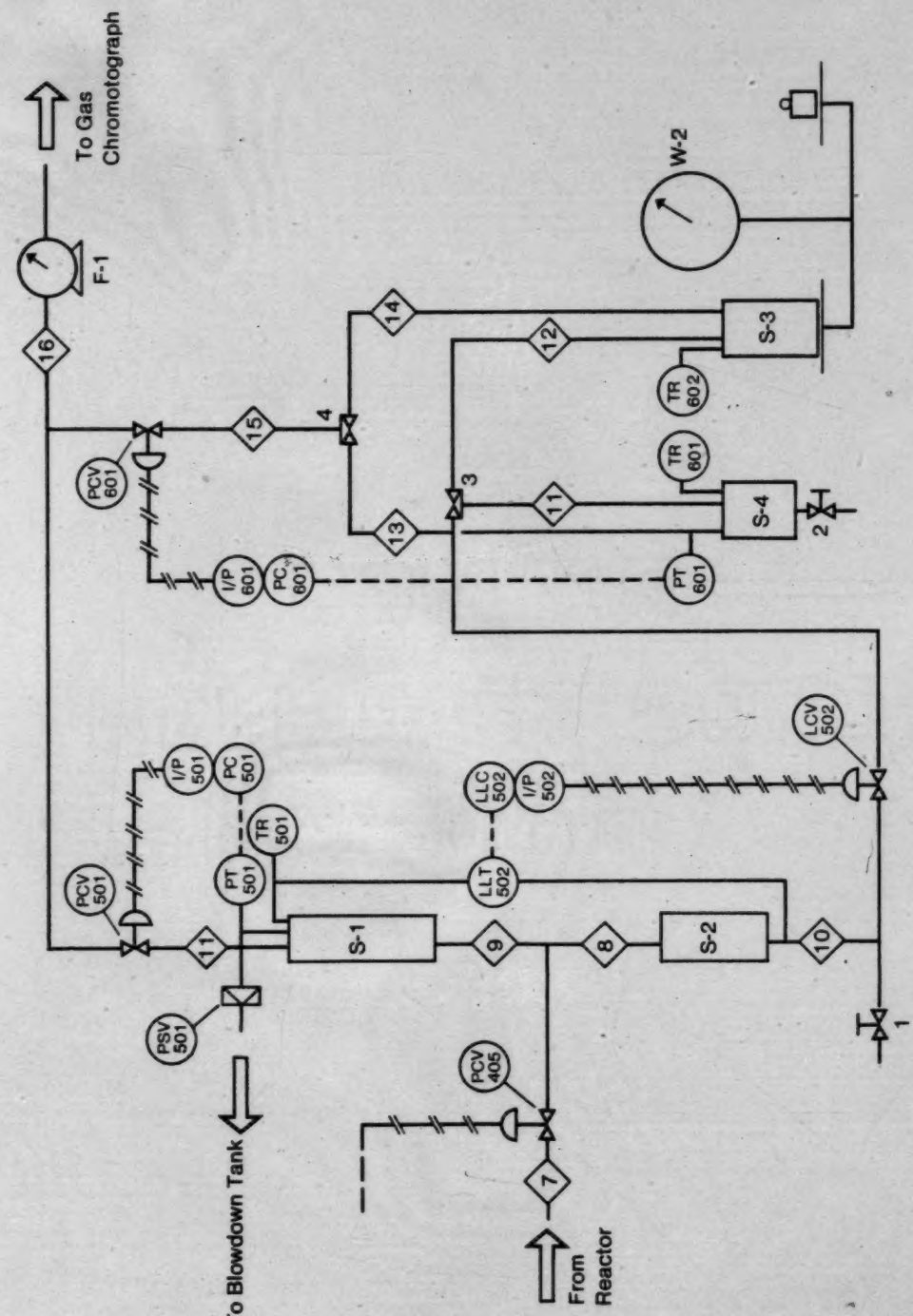


Figure 2: Separation Section

Symbols for Figure 2

1	Sample Valve
1A	Sample Valve
2	Drainage Valve
3	Three-Way Valve
4	Three-Way Valve
F-1	Dry Gas Test Meter
S-1	Upper High-Pressure Separator
S-2	Lower High-Pressure Separator
S-3	Product Tank
S-4	Auxiliary Product Tank
W-2	Scale

TABLE 1: CONTROL LOOPS IN HYDROCRACKING UNIT

CONTROL LOOP DESIGNATION	COMPONENTS		
	MEASUREMENT DEVICE	CONTROLLER	FINAL CONTROL DEVICE
1. Hydrogen Flow Control Loop 101	Beckman Model 864 Differential Pressure Transmitter FT-101	Beckman Model 8830 Controller, FT-101, c/w Foxoboro I/P Model 69TA-II Converter, I/P-101	Annin 5061 Control Valve, "Wee-Willie" c/w Size AA trim, FCV-101
2. Reactor Pressure Control Loop 401	Beckman Model 864 Pressure Transmitter, PT-401	Same as above, PC-401 & I/P-401	Annin 5061 Control Valve, "Wee-Willie" c/w Size A trim, PCV-401
3. Separator Pressure Control Loop 501	Beckman Model 864 Pressure Transmitter, PT-501	Same as above, PC-501 & I/P-501	Badger Model P786 Research Control Valve c/w Type TLDA Positioner, PCV-501
4. Liquid Level Control Loop 502	Beckman Model 864 Differential Pressure Transmitter LLT-502	Same as above, LLC-502 & I/P-502	Badger Model P785 Research Control Valve c/w Type BLRA Positioner, LCV-502
5. Separator Pressure Control Loop 601	Beckman Model 864 Pressure Transmitter, PT-601	Same as above, PC-601 & I/P-601	Badger Model P785 Research Control Valve c/w Type TLDA Positioner, PCV-601

flow element with a Beckman Model 861 differential pressure cell, FT-101. The laminar flow element is basically a section of 1.59 mm stainless steel capillary tubing, with an internal diameter of 0.254 mm. The pressure drop is used as the input signal to the hydrogen flow control loop 101 which controls the flow rate of hydrogen. In addition, a high pressure rotameter has been installed in line 3 so that the hydrogen flow rate can be visually monitored.

Temperature of the hydrogen feed is measured by a 0.10 m Thermo Electric SS316 Sheathed Type J Ceramo thermocouple, with immersion length of either 0.10 m, 0.13 m or 0.20 m.

The liquid feed is stored in a cubic tank made of stainless steel sheet metal. The feed tank is placed on a Toledo Scale Company scale, so that the weight of the tank and its contents can be continuously monitored.

Liquid feed is transferred from the feed tank to the reactor by a Milton Roy Instrument Duplex Mini Pump, P-1. The Mini Pump is a positive displacement pump capable of accurately delivering liquid at high pressure. The rated minimum and maximum capacities of the pump are 145 mL/h and 290 mL/h respectively. It is calibrated by measuring the liquid feed rate at the inlet of the pump. A 100 mL burette is connected into the feed line and is used for direct measurement of the volumetric flow rate of the liquid feed.

Reaction Section

The reactor used is a Magne Drive Packless Autoclave, R-1, manufactured by Autoclave Engineers Inc. A detailed diagram of the autoclave can be found in the manufacturer's operating manual.

The reactor consists of a bolted closure autoclave and an agitator. The autoclave has a volume of 0.3 L and a maximum working pressure of 37.3 MPa at 343°C. Mixing of the liquid and the gaseous reactants in the autoclave is provided by a specially designed Magne Drive Agitator. The agitator is belt-driven by a Impak V-S variable drive. Rotation speed of the agitator is measured by an Autoclave tachometer.

Reactor pressure is measured by both a Weiss pressure gauge, PI-403, and a Beckman Model 864 pressure transmitter, PT-405. The pressure of the reactor is maintained by back pressure control loop 401.

The autoclave is heated by an Autoclave high temperature furnace which has a capacity of 4.3 MJ/h. The furnace temperature is controlled by a Thermo Electric Selectrol Series 800 controller, which has a time based proportional with automatic reset mode. Reactor temperature is measured by a 0.20 m Thermo Electric Ceramo thermocouple.

The liquid feed enters the reactor from the top of the reactor cover via line 1, whereas the hydrogen stream is split into two: line 3 enters from the reactor top, and line 4, through the shaft of the Magne Drive Agitator.

The autoclave contains a safety head assembly, PSE-401, which is threaded into the body of the autoclave. The safety head assembly consists of a safety head body, a gasket, a rupture disc, a hold-down ring and a hold-down nut. It is connected to a blowdown tank by 0.64 cm stainless steel tubing. The Inconel rupture disc used has a rated rupture pressure of 39.5 MPa at 22°C.

A high reactor pressure safety action is supplied by a Murphy Switchgage, PSH-401, which will cut off the power to the liquid feed pump and the autoclave furnace when a pre-assigned reactor pressure is reached, generally 6.89 MPa above normal reactor pressure.

Separation Section

The mixture of liquid and gaseous products leave the reactor via line 7. Line 7 is a 0.32 cm stainless steel tubing that extends into the reactor and ends 2.5 cm above the impeller of the agitator. This ensures a constant liquid holdup. Line 7 is not insulated so that the products leaving the reactor are cooled down to ambient temperature before entering the lower high pressure separator, S-2.

S-2 is a 0.15 m Ferguson liquid level sight glass. The sight glass which has a small holdup volume, minimizes the retention time of the products. It also permits a visual inspection of the liquid level which is controlled by liquid level control loop 502.

Gas leaving S-2 enters the upper high pressure separator, S-1. S-1 provides an additional disengaging

volume for gas-liquid separation. A detailed diagram of S-1 can be found in Appendix A. The pressure in S-1 and hence, S-2, is maintained by back pressure control loop 501. The temperature in S-1 is measured by a 0.13 m Thermo Electric Ceramo thermocouple.

Liquid in S-2 is transferred to the low pressure separation system via line 10. A sample valve, SV-1, is located on line 10, so that liquid sample can be withdrawn from the bottom of S-2 for analysis. The low pressure separation system consists of a product tank, S-3, and an auxiliary product tank, S-4. Liquid from S-2 can be transferred to either S-3 or S-4 by means of a by-pass valving system.

The cylindrical product collection tank, S-3, is made of acrylic and has a holding volume of 1.34 L (See Figure A-2 in Appendix A). It is placed on a Toledo Scale Company scale so that its weight can be monitored continuously.

Tank S-4 is a QVF glass connector with stainless steel flanges on either end (See Figure A-3 in Appendix A). It has a smaller holding volume than S-3. Liquid content in S-4 can be withdrawn from the bottom flange. The pressure in S-4 is maintained at 6.89 KPa above atmospheric pressure, by back pressure control loop 601. Temperatures of S-3 and S-4 are measured with 0.13 m thermo Electric Ceramo thermocouples.

The exit gas from S-3, or S-4, combines with that from S-1 to form a single stream (line 16). The flow rate of the exit gas stream is measured with an American dry gas test

meter and its composition is determined by means of gas chromatography.

All the outputs of the thermocouples in the unit are visually displayed and recorded on Recorder 1, which is a Honeywell Electronik 16 recorder. Input signals to all the controllers in the unit are recorded on Recorder 2 which is a Honeywell Electronik 15 recorder.

B. Equipment Modification for Catalytic Hydroprocessing Studies

The reactor of the pilot unit is modified so that it can be used in studies of catalytic hydroprocessing of heavy gas oil. The modification involves the removal of the cooling coil and the addition of a stationary catalyst basket. The design of the catalyst basket is limited by the capacity and internal geometry of the autoclave. The basket is made of two concentric cylindrical walls, and completed with top and bottom cover plates (See Figure 3). It has a capacity of 4.77 mL. The inner cylindrical wall is made from 1.59 cm stainless steel tubing, while the outer wall is formed of 0.13 cm thick stainless steel plate perforated with 0.15 cm holes. Both walls are 1.10 cm high. The top and the bottom cover-plates are made of the same material as the outer cylindrical wall. They are held together by a pair of 0.15 cm studs and bolts. The interior of the catalyst basket is lined with a layer of stainless steel wire mesh. The basket is suspended from the reactor cover by a 0.32 cm

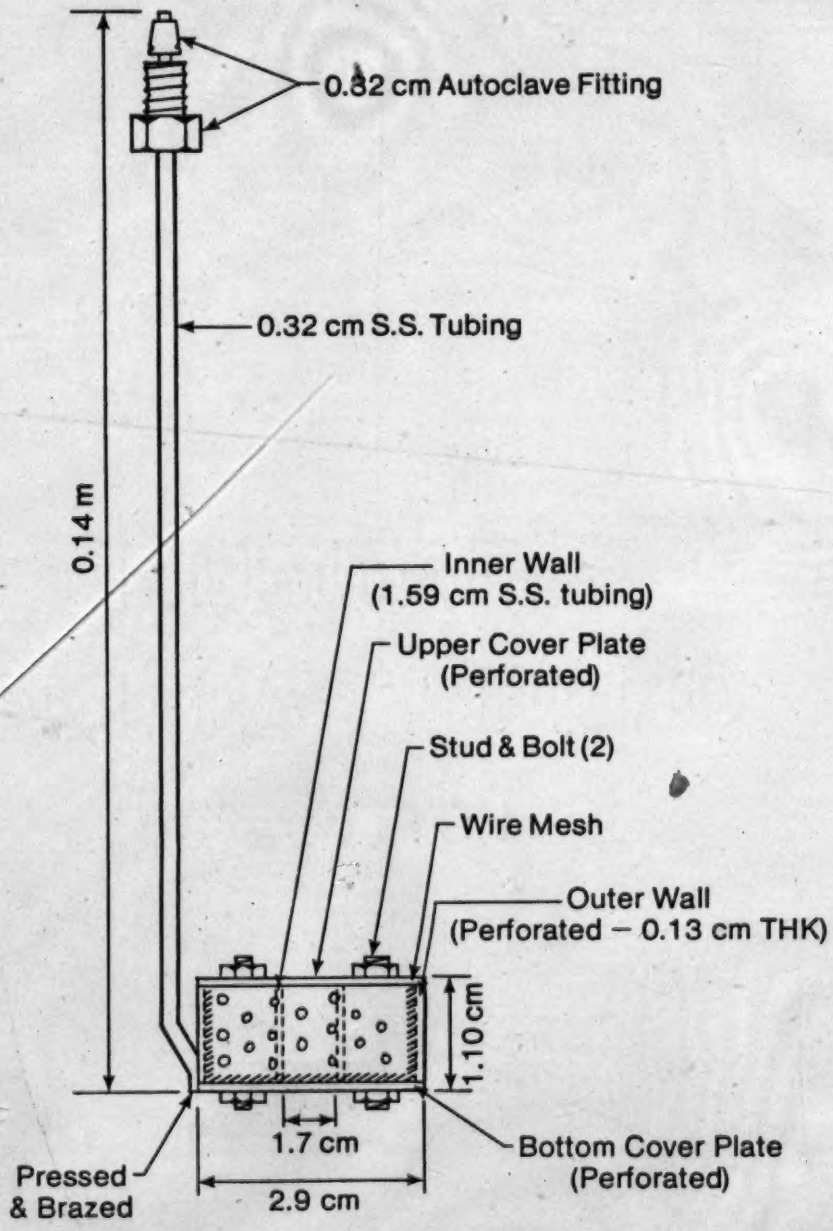


Figure 3: Catalyst Basket Assembly

stainless steel tubing and is located between the impeller and the inlet of the liquid product line. This is to ensure that the catalyst basket will be completed immersed in the reactor contents.

IV. OPERATION

The experiments involved reacting heavy gas oil with hydrogen under high pressure and high temperature.

The major operating variables to be monitored were reactor pressure, reactor temperature, liquid feed rate, liquid product rate, hydrogen feed rate, product gas flow rate and agitator speed.

A. Thermal

Prior to the start of a thermal hydroprocessing run, 0.12 L of heavy gas oil was placed in the autoclave reactor. This ensured that the inlet of the product line leaving the reactor was immersed in gas oil. After the autoclave was assembled, it was pressurized with hydrogen and checked for leaks. The reactor was considered to be leak-free when the drop in pressure in the isolated reactor was less than 70 KPa in half an hour. When the reactor system was found to be leak-free, hydrogen and heavy gas oil were introduced. Flow rates of hydrogen and heavy gas oil were adjusted until the desired values were reached. The agitator, which provided the mixing of hydrogen and heavy gas oil inside the reactor, was then started and set at 800 rpm. The agitator speed of 800 rpm was used because a Residence Time Distribution Study of the reactor system showed this speed was sufficiently high to provide perfect mixing. Minor adjustments were made to the settings of pressure controllers so that the desired reactor and separator pressures were maintained. The

temperature of the reactor was then raised gradually at 200°C per hour until the desired value was reached. Liquid and gaseous products, leaving the reactor, were depressurized in two stages. They were first cooled down to near ambient temperature, and then allowed to flash in high pressure separators that were maintained at 2.5 MPa. The liquid, leaving the high pressure separators, was further depressurized to 13.8 KPa, in a low pressure product tank. The gaseous product streams leaving the high pressure separators and the low pressure product tank were combined into one stream and transferred to a gas chromatograph for analysis.

Sampling of the liquid and the gaseous products began after the system had been running at steady state for over two hours. One milliliter liquid product samples were withdrawn periodically from the bottom of the lower high pressure separator. These samples were stored in capped vials. To minimize leakage of light hydrocarbons, the sample vials were stored in a refrigerator until analyses could be carried out. A larger sample of the liquid product (10 mL) was collected at the end of each run for density and sulfur content measurement. The gaseous product stream was analyzed as frequently as desired during the run by means of an on-line gas chromatograph.

Cumulative mass flows of the liquid feed and the liquid product were measured by scales. Volumetric flow rates of hydrogen feed and product gas were measured with the

American dry gas test meter; the former was taken prior to start of run, while the latter, during the run. Liquid holdup in the reactor was obtained by isolating the reactor before the complete shutdown of the system, and then measuring the liquid content inside the reactor when it had been cooled down to ambient temperature.

Detailed operating procedures, including startup and shutdown, can be found in Appendix B.

B. Catalytic

Prior to the start of a catalytic run, the basket was filled with a known weight of catalyst. Then the top cover-plate was replaced and the hold-down nuts were tightened up. Finally the whole agitator assembly, together with the catalyst basket, was placed into the reactor, which contained 60 mL of heavy gas oil (HGO). After the reactor system was found to be leak-free, the catalyst was ready to be conditioned according to manufacturer's recommendations. One day before the commencement of a catalytic run, the catalyst was conditioned via three stages:

1. Reduction under hydrogen atmosphere at 430°C and 10.3 MPa for two hours
2. Presulfiding with HGO containing 2% by volume of carbon disulfide at 430°C and 17.2 MPa for two hours
3. Aging with HGO at 430°C and 17.2 MPa for two hours.

Detailed description of the procedures for catalyst conditioning is provided in Appendix B.3.

In general, the conditioned catalyst was allowed to cool under hydrogen atmosphere overnight and the start of a catalytic run would begin the next day, following the same procedure as those developed for thermal hydrocracking. Sampling of liquid product began after the reactor system had been running at the desired operating condition for over two hours.

C. Residence Time Distribution

A basic assumption used in this study is that the reactor system behaves like a continuous stirred tank (CSTR). To verify the validity of this assumption, a residence time distribution (RTD) study was carried out on the reactor system, using a step change in tracer input.

The liquid feedstock used was Heavy Atmospheric Gas Oil (HAGO) supplied by the Imperial Oil Strathcona Refinery. It was chosen because of its narrow boiling range and stability. Physical properties of HAGO are listed in Table 2.

The primary tracer used in the RTD study was n-heptane and the secondary, n-heptadecane. They were added to a batch of HAGO. The concentration of n-heptane in HAGO, determined by means of Simulated Distillation Analysis (SDA), was the variable to be monitored. The concentration of the secondary tracer, n-heptadecane, was also determined but was neglected because of its poor response to SDA.

Boiling Range, °C	254-415
Specific Gravity at 15°C	0.846
Sulphur, wt.%	<0.02
Fractions, vol.%	
Naphtha (C_7-177°C)	--
Distillate (177-343°C)	53.0
Fuel Oil (343°C+)	47.0

TBP (by SDA)	
Volume %	°C
IBP	254
5	278
10	298
30	324
50	339
70	357
90	379
95	384
EP	415

Table 2: Physical Properties of HAGO

The reactor system was started up according to the normal startup procedures. The only deviation was that the HAGO was fed to the reactor from a burette instead of from the liquid feed tank. This was to minimize mixing at the interface during the period when HAGO containing the tracers was introduced.

The reactor system was operated at the following conditions:

Temperature	: 295°C
Pressure	: 13.8 MPa
LHSV	: 0.696 h^{-1}
H_2/oil	: 879 m^3API/m^3

The above operating conditions were selected because based on previous experience with the same liquid feedstock, these were the upper limits applicable without hydrocracking. To ensure hydrocracking was actually not occurring, the product gas stream was analyzed continuously. After the reactor system had stabilized at the above condition for two hours, the HAGO in the feed burette was allowed to decrease to a level as low as visually possible. Then, a special blend of HAGO containing the tracers, prepared prior to the start of run, was added to the burette. Extreme care was exercised to ensure minimum disturbance of the interface between the HAGO remaining in the burette and the HAGO containing the tracers. Liquid samples were then collected from the bottom of the lower high pressure separator at 10-minute intervals. The samples were stored in capped sample vials. They were

analyzed later on for their boiling point distribution. The reactor system was shut down after 32 samples, an equivalent of a run time of 5 hours, had been collected.

V. ANALYTICAL

The ability to interpret results from the operation of a hydroprocessing pilot plant was highly dependent on the analytical facility available. The liquid feed and product were normally analyzed for their boiling point distribution, density, sulfur content and nitrogen content. Conventionally, this information would be obtained by distillation (ASTM-D86, ASTM-D1160), hydrometer (ASTM-D287), combustion (ASTM-D1551) and digestion/titration methods. However, these methods were unsatisfactory because of either the large sample size or long analytical time required.

To replace the conventional methods, advanced analytical techniques and equipment were introduced. They included gas chromatography for boiling point distribution, X-ray florescence for sulfur content and the use of a densiometer for density measurement. A comparison of the conventional and the advanced analytical methods used in this study can be found in Table 3.

Furthermore, the gaseous product stream was analyzed by means of gas chromatography.

Following is a description of the analytical methods used in this study:

	CONVENTIONAL METHOD		PRESENT METHOD	
	SAMPLE SIZE	ANALYTICAL TIME	SAMPLE SIZE	ANALYTICAL TIME
1. DISTILLATION				
D-86	100mL	2h	--	--
D-1160	100mL	6h	--	--
TBP	1 to 5L	24h	5μL	3h
2. DENSITY	100mL	0.2h	10mL	0.5h
3. SULFUR CONTENT	1mL	5h	10mL	0.2h

Table 3: Comparison of Conventional and Present Methods of Characterizing Petroleum Products

A. Boiling Point Distribution (Simulated Distillation Analysis, SDA)

The boiling point distribution of liquid samples was obtained with a temperature programmed Hewlett-Packard Model 5830A gas chromatograph. A differential thermal conductivity detector was employed. Both the analytical and the reference gas chromatographic columns used were 0.45 m of Dexsil 300 GC on 80/100 mesh Chromsorb W. A detailed description of the principles involved and the operating procedure can be found in Appendix C. This analysis is referred to as Simulated Distillation Analysis (SDA).

The gas chromatograph was calibrated with a standard mixture of n-paraffins supplied by Poly Science Corporation, ranging from C9 to C40. A typical gas chromatogram of the calibration mixture is shown in Figure 4. The calibration was required to relate the boiling points of hydrocarbons eluting from the gas chromatographic column to their corresponding retention time.

Two chromatographic runs were needed to obtain sufficient data on one liquid sample: a blank run and a sample run. Both runs were carried out at the same chromatographic condition. The blank run was a run when nothing was injected into the chromatographic column. It was required to compensate for the baseline drift due to the difference between the reference and the analytical columns. The true chromatographic areas for the liquid sample were obtained by subtracting the chromatographic area of the

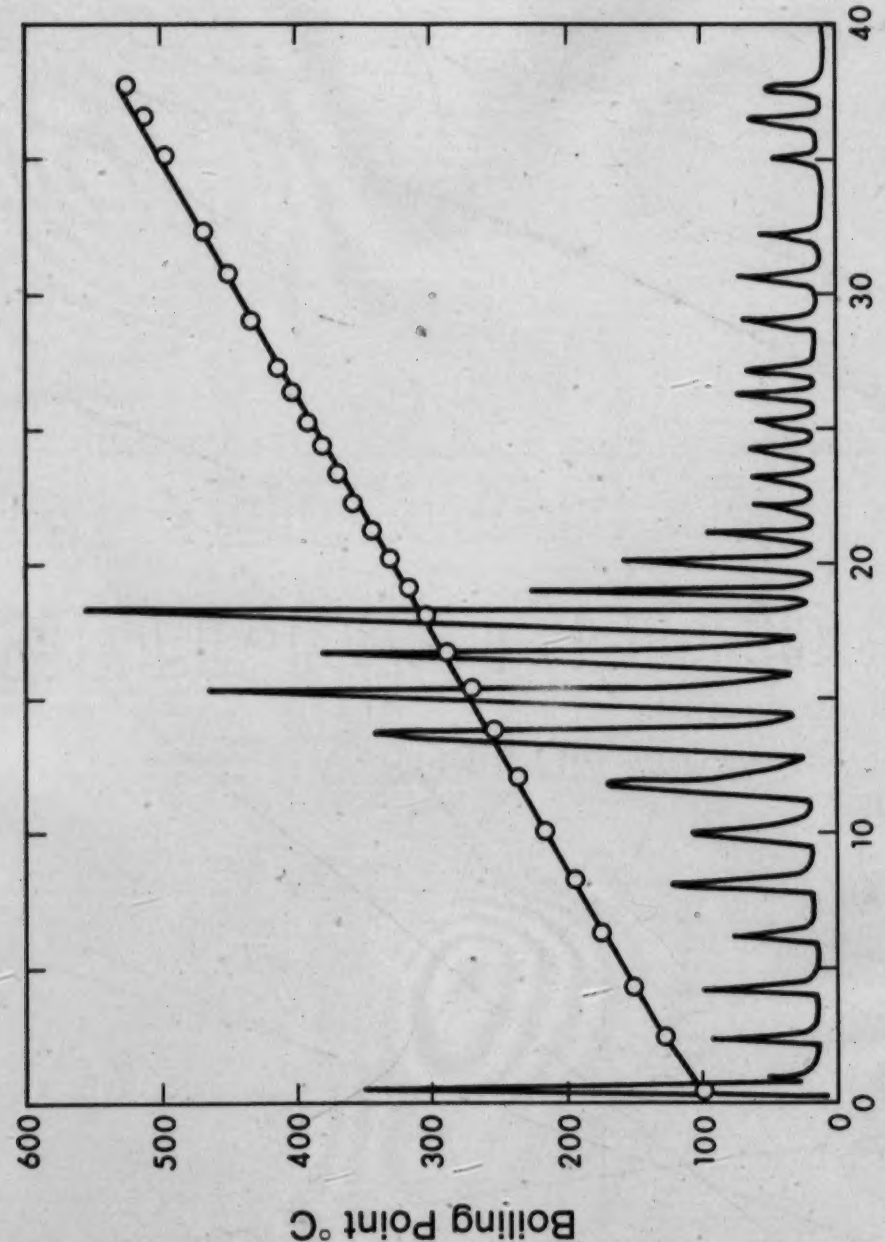


Figure 4: Typical Gas Chromatogram of Calibration Standard and Corresponding Boiling Point Correlation

blank run from that of the sample run. By assuming all the hydrocarbons in the liquid sample had the same response factor, the true cumulative chromatographic area was directly proportional to the cumulative volume of the sample eluted from the chromatographic column. A typical gas chromatogram of a liquid sample is shown in Figure 5.

NEWS1, a FORTRAN IV program was written to process the raw gas chromatographic data. A listing of this computer program can be found in Appendix D. A typical computer output is shown in Table 4. RT is the retention time, A is the chromatographic area of the sample run, L is the chromatographic area of the blank run, AL is the difference between A and L, whereas B.P. is the boiling point in °F.

B. Density

The density of liquid sample was measured with a Digital Precision Density Meter Model DMA 02C. The densimeter worked on the principle of variation in the natural frequency of a hollow oscillator when filled with different liquids. After calibrating with air and water, a liquid sample was introduced into the densimeter. The resulting change in the natural frequency of the hollow oscillator was used to calculate the density of the liquid sample.

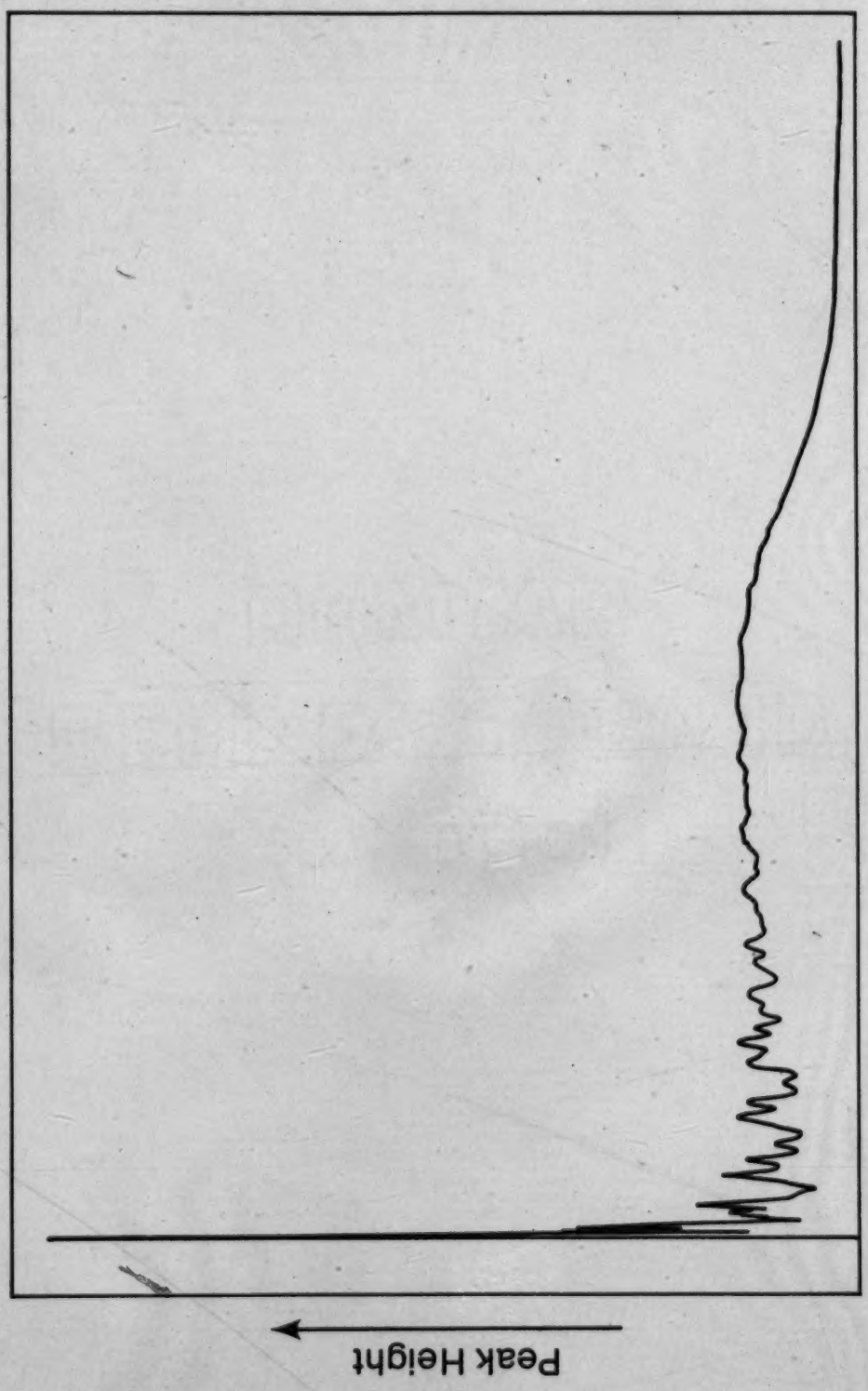


Figure 5: Typical Gas Chromatogram of Liquid Product

HP RUN # 346 OCT/03/79 TIME 15:19:24
ID:9752
AREA %

RT	AREA	AREA %
0.51	8978	9.030
1.51	3013	3.031
2.51	3191	3.210
3.51	2212	2.225
4.51	3405	3.425
5.51	2343	2.357
6.51	3490	3.510
7.51	3088	3.106
8.51	3356	3.376
9.51	3117	3.135
10.51	3352	3.372
11.51	3308	3.327
12.51	3586	3.607
13.51	3490	3.510
14.51	3721	3.743
15.51	3652	3.673
16.51	3730	3.752
17.51	3716	3.738
18.51	3907	3.930
19.51	3877	3.900
20.51	3857	3.880
21.51	3715	3.737
22.51	3558	3.579
23.51	3281	3.300
24.51	3002	3.020
25.51	2567	2.582
26.51	2105	2.117
27.51	1598	1.607
28.51	1185	1.192
29.51	848	0.853
30.51	553	0.556
31.51	340	0.342
32.51	191	0.192
33.51	49	0.049
34.51	13	0.013
35.51	5	0.005
37.51	11	0.011
40.51	10	0.010

DIL FACTOR: 1.0000 E+ 0

Figure 5 (Cont'd) : Typical Gas Chromatogram of Liquid Product

SAMPLE RUN NUMBER 9752
SAMPLE NAME SAMPLE # 9034-3
DATE 3 -10 - -79
BASELINE HP5730A RUN NUMBER 345
OIL HP5730A RUN NUMBER 346
HP5730A CALIBRATION STANDARD 9748
AREA OF REJECTION 0

RT	A	L	AL	VOL	ACC. VOL.	B. P.
.51	8978.	38.	8940.	9.550	9.550	222.16
1.51	3013.	53.	2960.	3.162	12.712	242.61
2.51	3191.	97.	3094.	3.305	16.017	263.07
3.51	2212.	144.	2068.	2.209	18.226	283.53
4.51	3405.	174.	3231.	3.451	21.677	303.99
5.51	2343.	226.	2117.	2.261	23.939	324.44
6.51	3490.	271.	3219.	3.439	27.377	344.90
7.51	3088.	261.	2827.	3.020	30.397	365.36
8.51	3356.	254.	3102.	3.314	33.711	385.81
9.51	3117.	298.	2819.	3.011	36.722	406.27
10.51	3352.	292.	3060.	3.269	39.991	426.73
11.51	3308.	234.	3074.	3.284	43.275	447.19
12.51	3586.	276.	3310.	3.536	46.810	467.64
13.51	3490.	258.	3232.	3.452	50.263	488.10
14.51	3721.	255.	3466.	3.702	53.965	508.56
15.51	3652.	253.	3399.	3.631	57.596	529.01
16.51	3730.	243.	3487.	3.725	61.321	549.47
17.51	3716.	252.	3464.	3.700	65.021	569.93
18.51	3907.	214.	3693.	3.945	68.966	590.38
19.51	3877.	175.	3702.	3.955	72.921	610.84
20.51	3857.	132.	3725.	3.979	76.900	631.30
21.51	3715.	149.	3566.	3.809	80.709	651.76
22.51	3558.	173.	3385.	3.616	84.325	672.21
23.51	3281.	167.	3114.	3.326	87.651	692.67
24.51	3002.	131.	2871.	3.067	90.718	713.13
25.51	2567.	117.	2450.	2.617	93.335	733.58
26.51	2105.	77.	2028.	2.166	95.502	754.04
27.51	1598.	102.	1496.	1.598	97.100	774.50
28.51	1185.	111.	1074.	1.147	98.247	794.96
29.51	848.	63.	785.	.839	99.086	815.41
30.51	553.	77.	476.	.508	99.594	835.87
31.51	340.	79.	261.	.279	99.873	856.33
32.51	191.	83.	108.	.115	99.988	876.78
33.51	49.	38.	11.	.012	100.000	897.24
34.51	13.	69.	0.	0.000	100.000	917.70
35.51	5.	40.	0.	0.000	100.000	938.16
36.51	0.	12.	0.	0.000	100.000	958.61
37.51	11.	33.	0.	0.000	100.000	979.07
38.51	0.	27.	0.	0.000	100.000	999.53
39.51	0.	30.	0.	0.000	100.000	1019.98

RT	VOL. PERCENT	B. P.
.03	.50	202.25
.27	5.00	207.16
1.14	10.00	225.07
4.51	20.00	294.04
7.87	30.00	362.67
11.00	40.00	426.79
13.92	50.00	486.54
16.65	60.00	542.22
19.26	70.00	595.73
21.81	80.00	647.95
24.77	90.00	708.34
26.77	95.00	749.30
30.81	99.50	832.08
34.00	100.00	897.24

Table 4 : Typical Simulated Distillation Result

C. Sulfur Content

The sulfur content of liquid samples was determined by X-ray fluorescence, using a Panalyzer 4000 manufactured by Panametrics, Inc. The radioactive source used in this instrument was Fe-55 isotope with a nominal activity of 20mCi. The instrument was consisted of two major components: a probe and an electronic console. The probe contained the radioactive source which emitted X-ray only in the direction of the sample. Radiation impinged on the sample caused it to emit X-rays which were characteristics of the emitting atoms. These X-rays were detected and converted to voltage impulses by a detector located behind the sample. The voltage impulses were transmitted to the electronic console which converted them into a digital display.

Ten milliliters of the liquid sample were placed in a sample holder lined with Mylar film. It was essential that the holder was filled to a minimum depth of 5 mm. The sample holder was then placed on the probe and was subjected to X-ray impingement as soon as it was safely insulated. The number of voltage impulses in a pre-set measurement time were compared with those for calibrated standards to obtain the sulfur content in the sample.

D. Bromine Number

An apparatus had been assembled for the determination of the "Bromine Number of Petroleum Distillates and Commercial Aliphatic Olefins by Electrometric Titration" ---

ASTM-D1159. A detailed description of the analytical method and the equipment required can be found in the 1977 Annual Book of ASTM Standards for Petroleum Products and Lubricants. The bromine number provides an indication of the percentage of unsaturated constituents in the liquid sample. For example, n-hexane has a bromine number of 0 and 1-hexene has a bromine number of 181.

E. Spinning Band Distillation

A Nester/Faust spinning band distillation column was used to obtain the true boiling point distribution (TBP) of liquid samples. Because of the large number of theoretical plates available, the spinning band distillation closely approximates a true boiling point distillation. It was used to demonstrate that SDA provided a reasonable approximation of TBP. Occasionally, it was employed in obtaining the specific gravity distribution of the various boiling fractions.

The distillation apparatus consisted of a sample pot, an annular column, a rotating spiral band, a heating mantle and a vacuum system. The original teflon spiral band was replaced by a stainless steel one so that it could stand up to the high temperature encountered.

After introducing 100 mL of liquid sample into the sample pot, the distillation column was placed under a vacuum of less than 1.3 KPa. The temperature of the sample pot was increased gradually by means of the heating mantle.

Overhead samples of the distillation were collected and removed at regular intervals for further analysis, while the corresponding overhead temperatures were recorded. When the gravity distribution of the liquid sample was desired, the density of the overhead samples were determined by densiometer.

F. Nitrogen Content

The nitrogen content of liquid samples was determined by a digestion distillation method, using a Kjeldahl system manufactured by Tecator Company. The system was comprised of two separate units:

1. Digestion Unit -- Digestion System 6
2. Distillation Unit -- Kjeltec System 1002 Distilling Unit

A weighed quantity of liquid sample was placed in a digestion tube in the Tecator Digestion System and concentrated sulfuric acid, hydrogen peroxide and a salt/catalyst mixture, which was supplied by Tecator Company as Kjeltab, were added. The digestion tube was electrically heated and maintained between 390 to 400°C for an hour. During digestion, organic compounds were converted to mainly ammonium sulphate, carbon dioxide and water.

After digestion, the sample solution was transferred to the distilling unit. In the distilling unit, ammonia was distilled from the sample solution after the addition of sodium hydroxide which converted ammonium sulphate to

ammonia and steam. The ammonia liberated during distillation was collected in boric acid solution. The boric acid solution was titrated with concentrated hydrochloric acid, to determine the amount of ammonia present. The nitrogen content of the liquid sample could then be calculated from the quantity of ammonia collected.

G. Refinery Gas Analysis (RGA)

Gas samples were analyzed with an automated gas chromatographic system installed in an Hewlett-Packard (HP) Model 5840A gas chromatograph. The system was capable of providing an analysis of the composition of fixed gases and light hydrocarbon in a refinery type of gas, which was referred to as Refinery Gas Analysis (RGA).

The following items were added to the HP-5840A gas chromatograph in order to make up the automated system:

1. Two 6-port and one 10-port switching valves;
2. Two Nupro needle valves;
3. Three analytical and one reference gas chromatographic columns
   a. Analytical columns:
      1) 7.32 m of 16% bis-2-methoxyethyl adiapate on 80/100 P-AW and 1.52 m of 30% DC 200 silicone oil on 80/100 Chromsorb P-AW
      2) 1.83 m of Porapak Q, 80/100 mesh
      3) 3.04 m of molecular sieve 5A, 60/80 mesh

b. Reference columns:

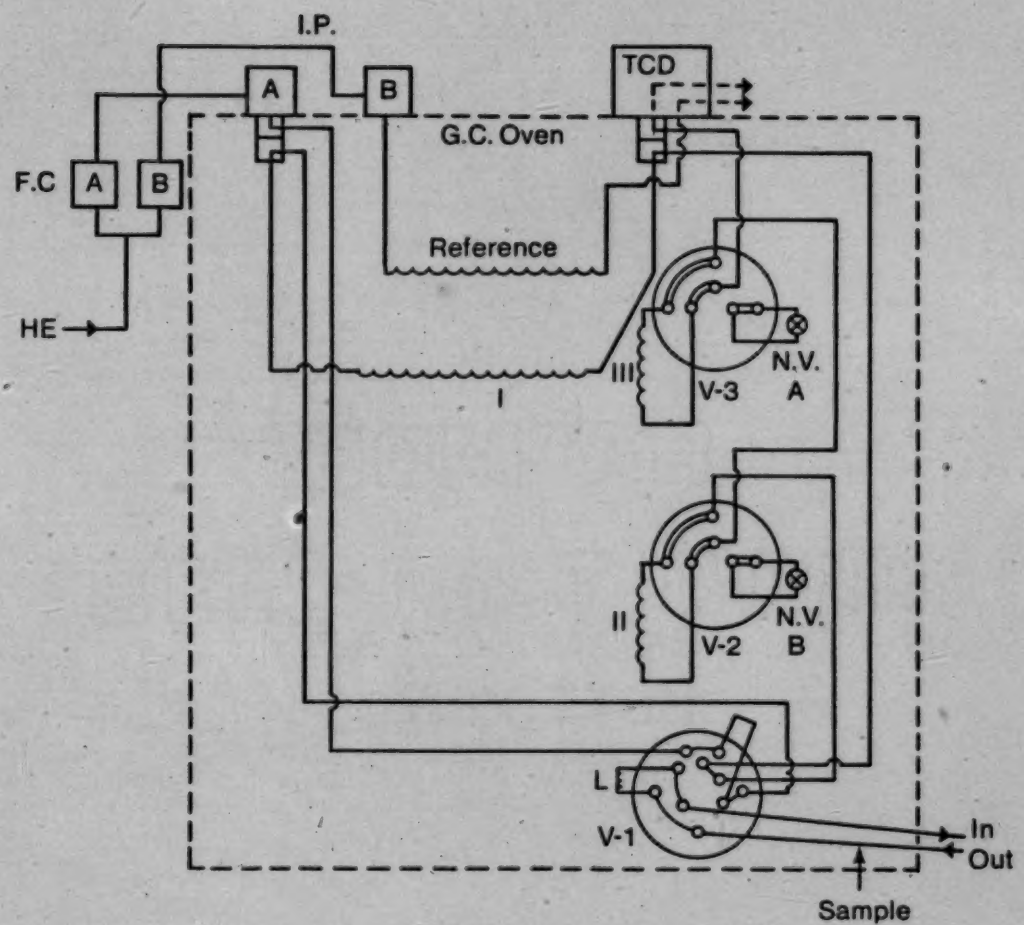
1) 0.51 m of 10% UCW-892 silicone on 80/100 Chromsorb W-HP

Figure 6 shows a schematic diagram of the gas chromatographic system, and Figure 7 shows the sequence of valve switching required.

The carrier gas used was a mixture of hydrogen and helium, containing 8.5 volume percent of hydrogen, supplied by Consumer Gas. This special blend of carrier gas was required to eliminate the dual-peak phenomenon of hydrogen. When pure helium was used as carrier gas, the hydrogen appeared as two adjacent peaks on the gas chromatogram, which resulted in significant error when the areas under the two peaks were being integrated. However, when the special blend of hydrogen and helium was used, this source of error was eliminated because the hydrogen would then appear as a single peak.

The gas chromatographic system was calibrated with a standard gas mixture supplied by Matheson Gas. The standard gas mixture was used to obtain the response factor of individual hydrocarbon present in the mixture. Its composition is listed in Table 5.

Typical gas chromatograms of the standard gas mixture and the gas product stream are shown in Figures 8 and 9 respectively.



Column I	Adipate + Silicone	FC	Flow Controller
Column II	Porapak Q	NV	Nupro Valve
Column III	Molecular Sieve 5A	L	Loop, 0.25 ml
		IP	Injection Port

Figure 6: Gas Chromatographic System for Refinery Gas System

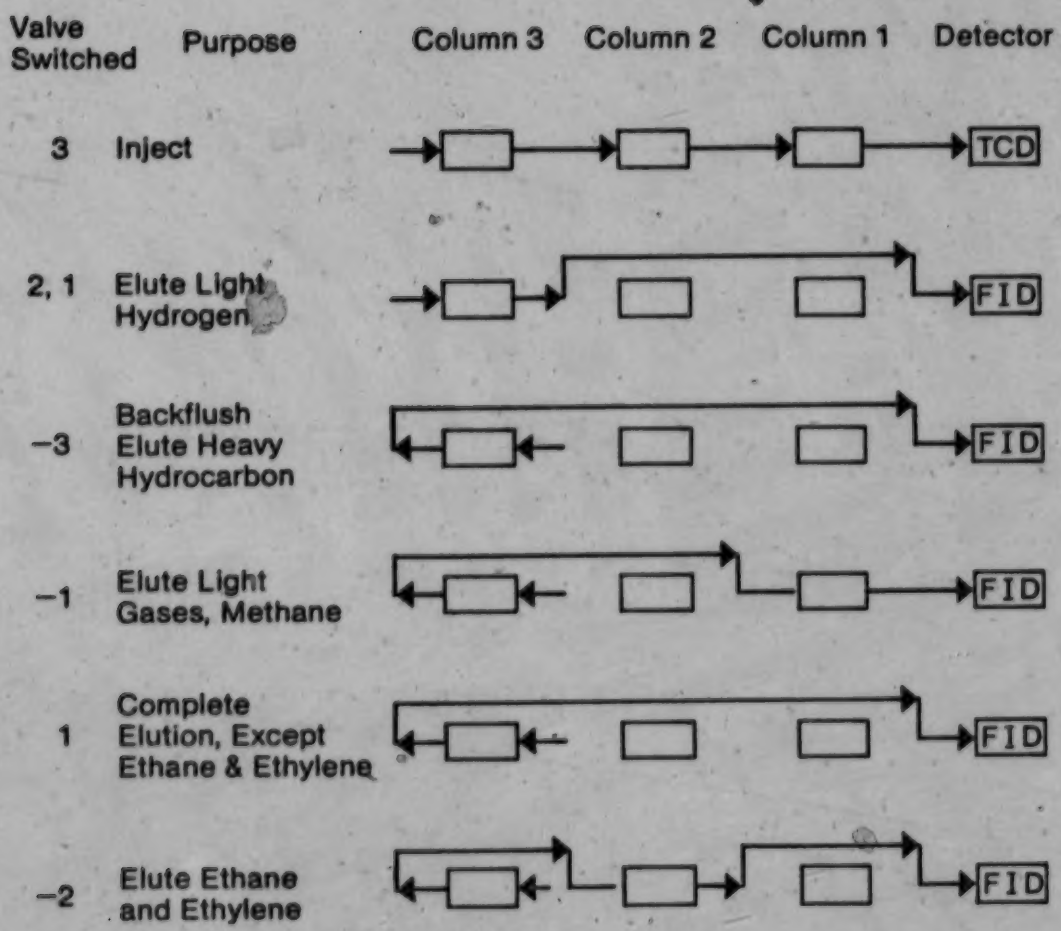


Figure 7: Sequence of Valve Switching in G.C. System for RGA

COMPONENT	VOLUME %
Hydrogen	88.50
Methane	1.02
Ethane	0.96
Ethylene	1.01
Propane	0.99
n-Butane	0.99
i-Butane	1.05
1-Butene	1.01
c-2-Butene	0.63
t-2-Butene	0.98
Pentane	0.94
2-Methyl-pentane	0.96
Hexane	0.96

Table 5: Composition of Standard Gas Mixture for Refinery Gas Analysis

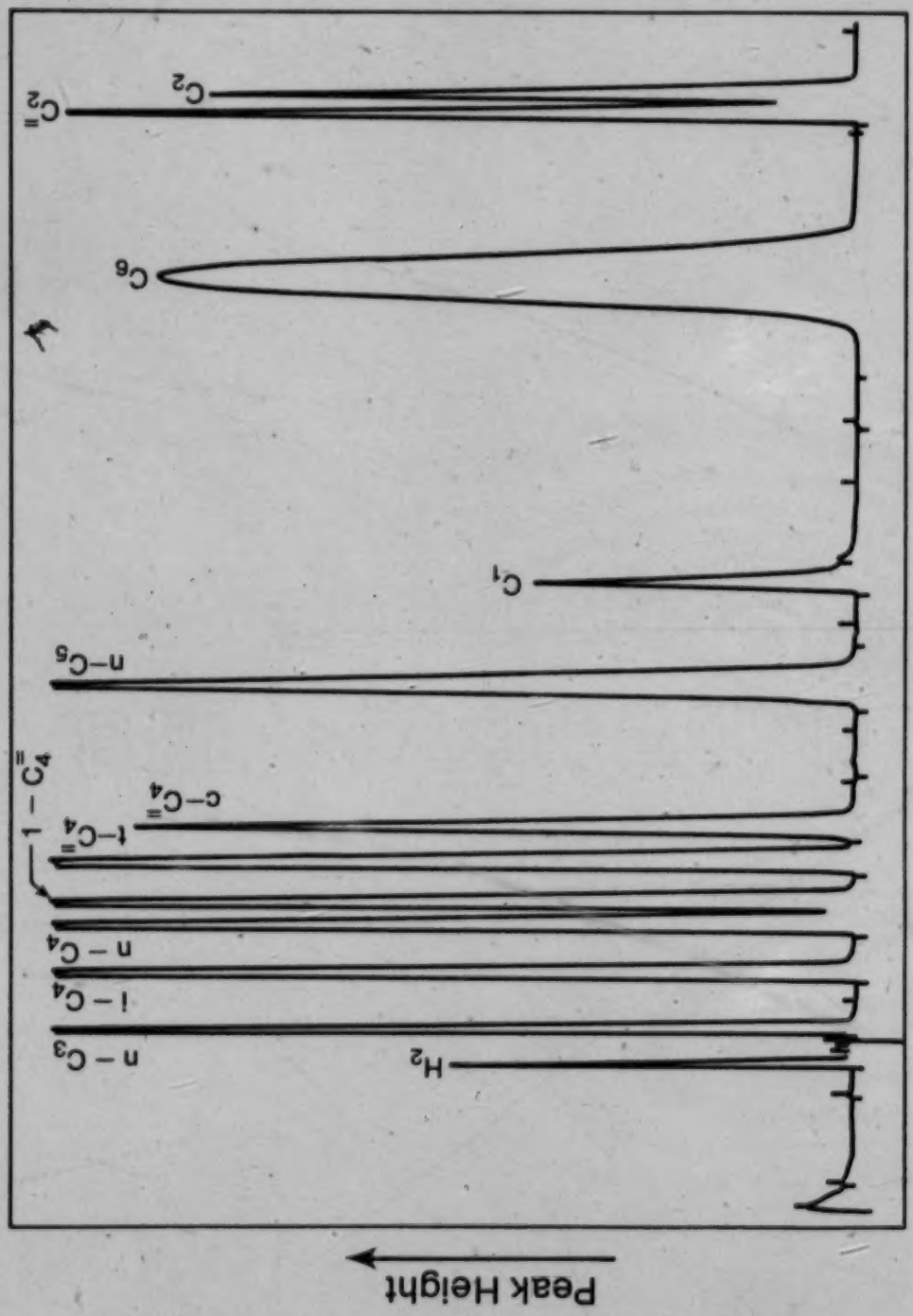


Figure 8: Typical Gas Chromatogram of Standard Gas Mixture

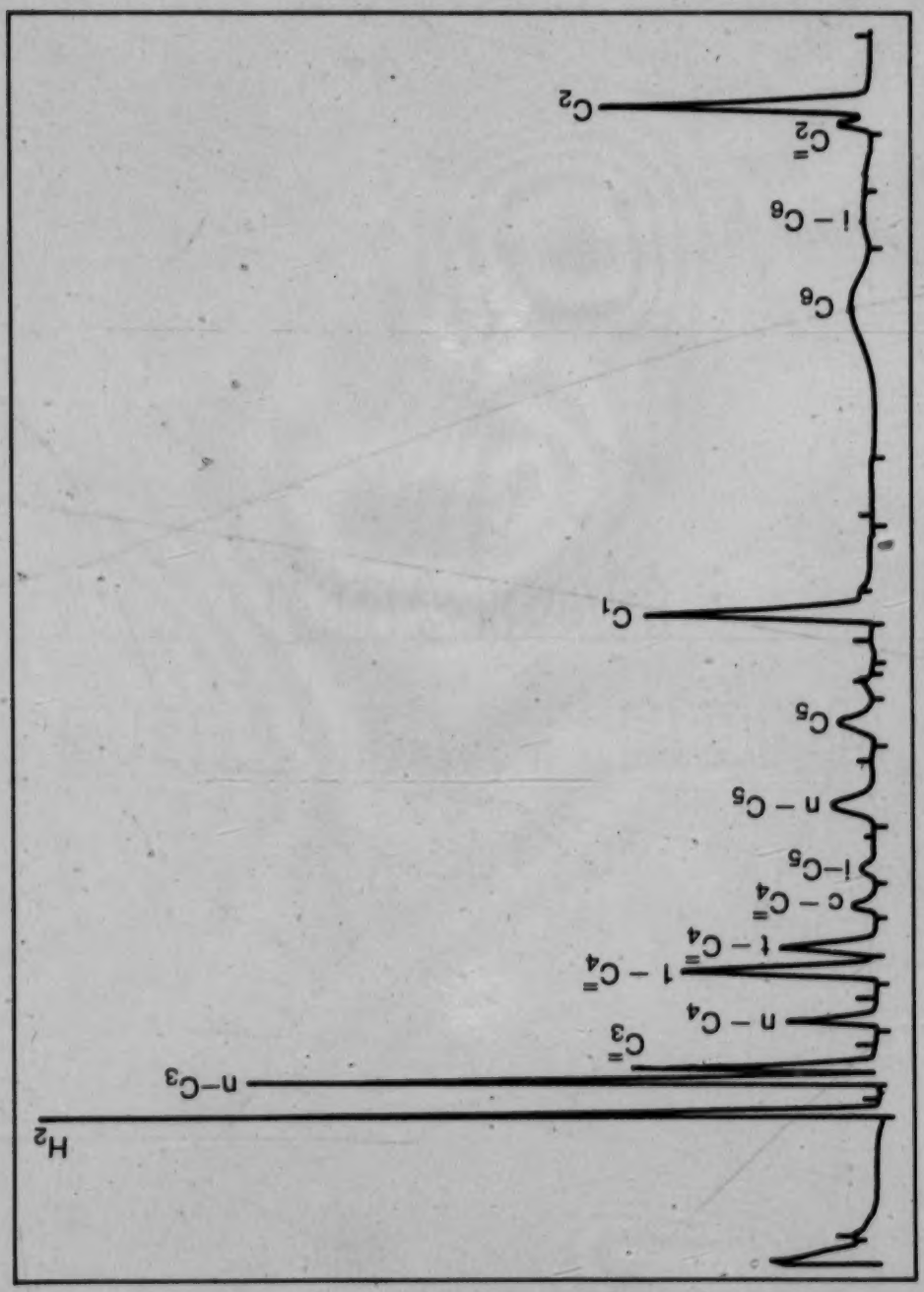


Figure 9: Typical Gas Chromatogram of Gaseous Product

H. Hydrogen Sulfide Content

The hydrogen sulfide content of product gas streams was obtained by the absorption/iodimetric method. The product gas stream to be analyzed was allowed to pass through 50 mL of 1.0 N caustic solution for fifteen minutes, where hydrogen sulfide would be converted to sodium sulfide.

$$2NaOH + H_2S \longrightarrow Na_2S + 2H_2O$$

The absorption solution was then acidified with sulfuric acid before iodine solution was added. The final solution was titrated against standard sodium thiosulphate, using fresh starch as indicator. This iodimetric method utilized the following reversible reaction:

$$S^{=} + I_2 \rightleftharpoons 2I^{-} + S$$

The hydrogen sulfide content could be calculated from the quantity of sodium thiosulphate required for titration.

VI. RESULTS

The continuous flow stirred tank reactor system (CSTR) was used to study the thermal hydrocracking of a heavy gas oil (HGO) derived from thermally hydrocracked Athabasca bitumen. The gas oil was supplied by the Energy Research Laboratories of CANMET. Typical analysis of the HGO can be found in Table 6. Boiling point distribution of the HGO is shown in Figure C-2. The hydrogen used was 99.9% pure and was supplied by Linde Division of Union Carbide.

Altogether twelve experimental runs were conducted. The average length of each run was five hours at steady state operating condition. All runs were carried out at a reaction temperature of approximately 450°C. Two levels of reaction pressure were examined, 13.8 MPa and 17.2 MPa. The ranges of liquid hourly space velocity studied were 2.1 to 5.1 h^{-1} at 13.8 MPa and 1.0 h to 3.5 h^{-1} at 17.2 MPa, respectively. The hydrogen to oil ratio was usually maintained within the range of 200 - 600 m^3API/m^3.

In this study, liquid hourly space velocity was defined as the hourly volume flow rate of liquid feed per unit volume of reactor liquid holdup. The reactor liquid holdup was the liquid content of the reactor, measured at the end of each run and normalized to a standard condition of 15°C and 101.3 KPa. The measurement of the reactor liquid content was necessary for each run because it was found to be dependent on the reaction temperature, pressure, LHSV, and

Boiling Range, °C	132 - 491
Specific Gravity 15°C	0.9148
Sulphur, wt.%	2.00
Nitrogen, wt.%	0.05
Bromine Number	9
Fractions, vol.%	
Naphtha (C_7 - 177°C)	5.6
Distillate (177 - 343°C)	50.1
Fuel Oil (343°C+)	44.3

Table 6: Typical Analysis of Liquid Feed
(CANMET HGO)

hydrogen to oil ratio. Hydrogen to oil ratio was defined as the volumetric flow rate of hydrogen feed at API standard condition (15°C and 101.3 KPa) per unit volumetric flow rate of liquid feed at 15°C.

The liquid products were analyzed for their boiling point distribution, density, sulfur content, nitrogen content and bromine number. The gaseous products were analyzed for composition (hydrogen, hydrogen sulfide and hydrocarbons up to hexane). The analyses of the liquid and the gaseous products for each run are listed in Tables 7 and 8. The detailed experimental data are listed in Appendix F.

A residence time distribution (RTD) study was carried out on the reactor system used in this study. The liquid feedstock used was a Heavy Atmospheric Gas Oil (HAGO) supplied by the Imperial Oil Strathcona Refinery. The tracers, applied to the liquid, were n-heptane and n-heptadecane. The RTD study was carried out at a pressure of 13.8 MPa and temperature of 295°C, a liquid hourly space velocity of 0.696 h^{-1} and a hydrogen to oil ratio of 879 m^3API/m^3. As soon as the reactor system had reached the above condition for two hours, a step change was introduced by feeding HAGO containing tracers. Samples of liquid leaving the reactor were collected at 10-minute intervals, and analyzed. Concentrations of the n-heptane tracer in the liquid samples collected are shown in Table 9.

The tracer used in the RTD study, n-heptane, has a boiling point of 98°C, whereas HAGO had an initial boiling

Run Number	9032	9035	9031	9030	9029
Operating Conditions:					
Pressure, MPa	13.8	13.8	13.8	13.8	13.8
Temperature, °C	449	450	450	450	449
LHSV, h^{-1}	2.11	2.19	2.55	3.27	5.07
H2/Oil, m^3API/m^3	300	290	360	410	590
Agitator Speed, rpm	800	800	800	800	800
Hydrogen Consumption, m^3API/m^3	39	36	--	26	--
Liquid Product					
Specific Gravity(15°C)	0.8758	0.8750	0.8816	0.8819	0.8929
Sulphur, wt.%	1.44	1.46	1.48	1.55	1.66
Nitrogen, wt.%	0.02	0.02	0.03	0.03	0.03
Bromine Number	25	25	26	26	23
Fractions, vol.%					
Naphtha(C7-177°C)	28.7	27.7	24.3	19.7	19.2
Distillate(177-343°C)	50.5	52.6	52.9	56.6	54.2
Fuel Oil(343°C+)	20.8	19.7	22.8	23.7	26.6
Gas Products, m^3API/m^3 (on a H2-free basis)					
C1	13.65	11.98	10.01	9.32	5.44
C2	7.95	7.04	6.21	5.75	3.69
C3	6.18	7.23	5.51	4.30	3.96
C4	2.75	2.47	2.70	2.25	2.42
C5	0.78	0.67	0.80	0.73	0.94
C6	0.39	0.38	0.40	4.10	0.67
H2S	4.91	5.61	6.01	5.62	5.44
Liquid Yield					
Volume %	99.3	100.3	99.1	98.6	101.6
Weight %	95.0	95.9	95.9	95.0	99.2

Table 7: Experimental Results of Thermal Hydroprocessing at 13.8 MPa

Run Number	9037	9022	9034	9033	9027	9036	9028
Operating Conditions:							
Pressure, MPa	17.2	17.2	17.2	17.2	17.2	17.2	17.2
Temperature, °C	452	449	449	451	447	450	448
LHSV, h^{-1}	1.34	2.15	2.31	2.73	2.92	3.06	3.50
H2/Oil, m^3API/m^3	450	247	361	326	348	330	350
Agitator Speed, rpm	800	800	800	800	800	800	800
Hydrogen Consumption, m^3API/m^3	297	83	50	--	67	--	20
Liquid Product							
Specific Gravity(15°C)	0.8651	0.8803	0.8784	0.8876	0.8788	0.8806	0.8807
Sulphur, wt.%	1.52	1.52	1.42	1.47	1.52	1.62	1.56
Nitrogen, wt.%	0.08	0.08	0.01	0.02	0.03	0.02	0.04
Bromine Number	25	20	24	22	21	24	23
Fractions, vol.%							
Naphtha(C7-177°C)	41.7	30.1	24.7	23.9	20.8	25.9	24.2
Distillate(177-343°C)	44.5	50.0	53.1	53.1	57.3	52.5	53.3
Fuel Oil(343°C+)	13.8	19.9	22.2	23.0	21.8	21.6	22.5
Gas Products, m^3API/m^3 (on a H2-free basis)							
C1	35.38	1.93	9.31	7.80	8.22	10.82	6.90
C2	18.16	1.10	5.77	5.50	4.89	6.70	4.40
C3	10.36	0.92	5.26	5.61	4.32	10.49	3.57
C4	4.17	0.37	2.53	3.30	2.24	2.91	1.84
C5	0.94	0.09	0.81	0.99	0.78	2.91	0.65
C6	0.40	0.09	0.40	0.77	0.52	0.47	0.42
H2S	5.11	3.21	5.06	6.48	4.32	5.95	4.52
Liquid Yield							
Volume %	98.5	104.2	100.1	97.0	100.7	100.3	100.5
Weight %	93.1	100.1	96.0	94.1	96.7	96.9	96.7

Table 8: Experimental Results of Thermal Hydroprocessing at 17.2 MPa

TIME minute	CONCENTRATION of C_7, C,	$\frac{C}{C_o}$
0	0.000	0.000
10	0.000	0.000
30	0.000	0.000
40	0.235	0.050
90	2.267	0.481
140	3.089	0.655
190	3.851	0.817
240	4.048	0.861
260	4.840	1.027
290	4.710	0.999

Table 9: Residense Time Distribution Study --- Response of Reactor System to Step Change in Tracer Input

point of 254°C. Therefore, the gas chromatogram of a sample of HAGO containing n-heptane gives two major peaks. The first major peak to appear is that of n-heptane (See Figure 10). In fact, n-heptane appeared as dual peaks in the chromatogram. This may be due to the impurities present in the reagent grade of n-heptane used. By assuming the response factor of n-heptane is the same as that of other hydrocarbons in HAGO, the concentration of n-heptane in HAGO (C) could easily be calculated from the areas under the n-heptane peak (CA_{C_7}) and the HAGO peak (CA_{HAGO}) in the chromatogram,

$$C = \frac{CA_{C_7}}{CA_{C_7} + CA_{HAGO}} \qquad (6.1)$$

Altogether four catalytic runs were carried out. The liquid (HGO) and the gaseous (hydrogen) feedstocks were the same as those used for thermal hydroprocessing runs. Two types of catalyst were used, Nalco 506 (Run 9038 and Run 9040) and Nalco 502 (Run 9041 and Run 9042). Both Nalco 506 and Nalco 502 are nickel molybdate on 0.16 cm extrudate of alumina support. Detailed chemical analysis and physical properties of the two catalysts are given in Table 10. For Runs 9038 and 9040, 3.15 g of catalyst were used, while for runs 9041 and 9042, 2.21 g. The operating conditions for each catalytic run, together with the analyses of the liquid and the gaseous products, are shown in Table 11.

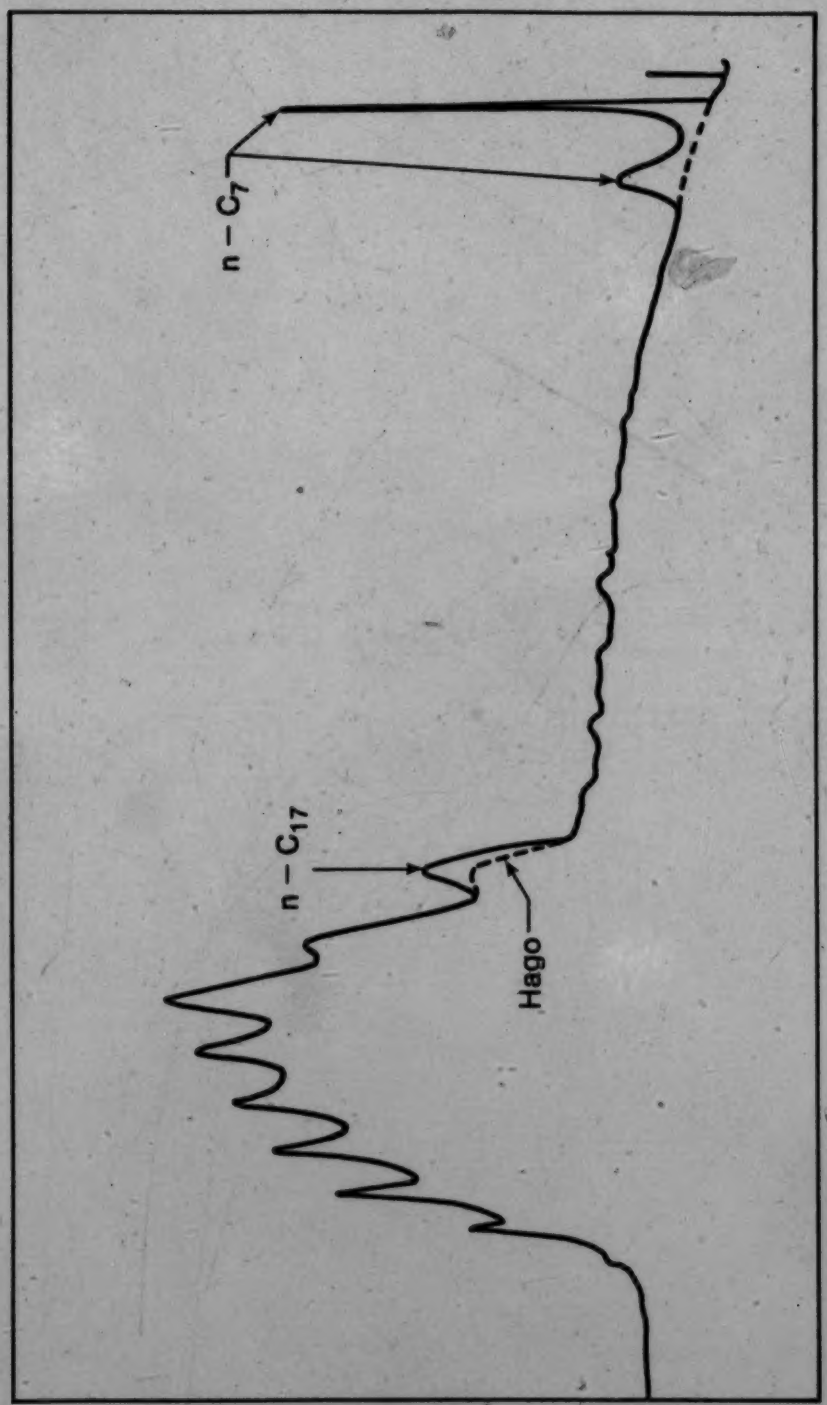


Figure 10: HAGO with Tracers

	Nalco 502	Nalco 506
Chemical Analysis, wt.% dry basis		
MoO_3	14.0	27.0
NiO	3.0	6.7
Na_2O	0.08	--
Fe	0.03	--
SiO_2	1.5	--
Al_2O_3	Balance	Balance
Physical Properties		
Form	Extrudate	Extrudate
Size, cm x cm	0.32x0.16	0.25x0.16
Surface Area, m^2/g	260	220
Pore Volume, mL/g	0.57	0.39
Density (Packed) g/mL	0.55	0.92
Strength, kg crush	6.8	6.3

Table 10: Analyses of Commercial Hydroprocessing Catalysts, Nalco 502 and Nalco 506

Run Number	9038	9040	9041	9042
Operating Conditions:				
Pressure, MPa	17.2	17.2	17.2	17.2
Temperature, °C	449	451	400	425
LHSV, h^{-1}	1.77	1.98	0.69	1.04
H2/Oil, m^3API/m^3	372	313	271	416
Agitator Speed, rpm	800	800	800	800
Catalyst Type	Nalco506	Nalco506	Nalco502	Nalco502
Catalyst Weight, g	3.15	3.15	2.21	2.21
Hydrogen Consumption m^3API/m^3	163	28	45	128
Liquid Product				
Specific Gravity at 15°C	0.8382	0.8426	0.8719	0.8540
Sulphur, wt.%	0.00	0.07	0.23	0.23
Nitrogen, wt.%	0.03	0.04	0.03	0.02
Bromine Number	8	11	6	9
Fractions, vol.%				
Naphtha (C7-177°C)	40.9	39.4	15.3	25.8
Distillate (177-343°C)	49.1	48.5	57.5	56.9
Fuel Oil (343°C+)	10.0	12.1	27.2	17.3
Gas Products, m^3API/m^3 (H2 - free basis)				
C1	13.28	14.75	2.78	7.69
C2	8.42	9.47	1.72	4.72
C3	5.79	7.71	1.72	4.04
C4	2.89	3.79	0.93	2.02
C5	0.79	1.08	0.26	0.54
C6	0.39	0.54	0.26	0.40
H2S	15.26	17.05	17.23	17.67
Liquid Yield				
Volume %	103.3	100.0	101.1	102.3
Weight %	94.6	92.0	96.5	95.5

Table 11: Experimental Results of Catalytic Hydroprocessing at 17.2 MPa

VII. DISCUSSION OF RESULT

A. Residence Time Distribution (RTD) Study

Figure 11 shows the RTD result obtained, together with the theoretical response of a continuous stirred tank reactor (CSTR) to a step change of input. The latter can be expressed as

$$X = \frac{C}{C_o} = 1 - \exp\left[\frac{t - d}{(1/LHSV)}\right] \qquad (6.2)$$

$$= 1 - \exp\left[\frac{t - 0.583}{1.45}\right]$$

where C_o = concentration of n-heptane in liquid sample at $t = \infty$

C = concentration of n-heptane in liquid sample at $t = t$

t = time, h

d = time delay, h

The parameters, d and (1/LHSV), were obtained by minimizing S^2, the square of the difference between measured and predicted (C / C_o),

$$S^2 = \left[(C/C_o)_m - (C/C_o)_t \right]^2 \qquad (6.3)$$

The agreement between the predicted and the measured values was reasonable. Furthermore, the measured LHSV was 0.690 h^{-1}, compared with 0.696 h^{-1} obtained from the best

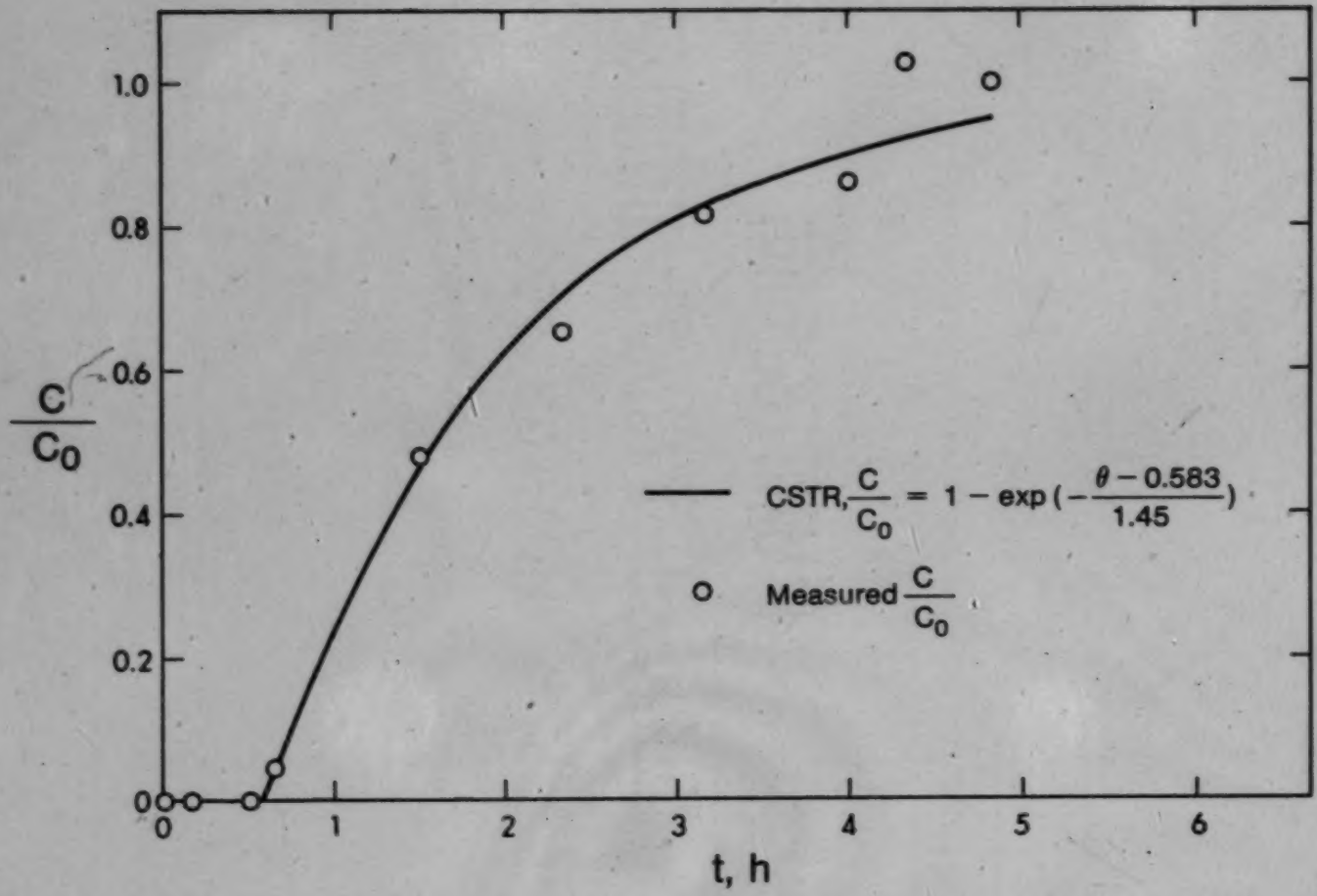


Figure 11: Residence Time Distribution of Study --- Response of Reactor System to a Step Change in Tracer Input

fit. Finally, the time delay of 0.583 h could be explained by the distance between the burette and the reactor.

Consequently, this RTD run indicated that the assumption of the reactor system used was a CSTR was a valid one.

B. Effect of LHSV on Product Composition

The product distributions at various LHSV are shown in Figures 12 to 15. Figures 12 and 14 illustrate the effect on the gaseous product and liquid product at 13.8 MPa and Figures 13 and 15 show the effect at 17.2 MPa.

At 13.8 MPa, the LHSV had a small effect on the composition of gas product over the range of one to three. However, the effect was more pronounced at 17.2 MPa; the percent of lighter component increased as the LHSV decreased. This was an indication that the extent of hydrocracking was greater at lower space velocities which is what one would expect.

Based on the SDA, the liquid samples were considered to be composed of three fractions: naphtha, distillate and fuel oil. The naphtha fraction was the fraction with a boiling point less than 177°C, the distillate fraction was the fraction with a boiling range of 177 to 343°C and the fuel oil fraction was the fraction with a boiling range above 343°C. As the LHSV decreased, the naphtha fraction increased while the fuel oil fraction decreased. The distillate fraction, however, remained relatively constant. This was

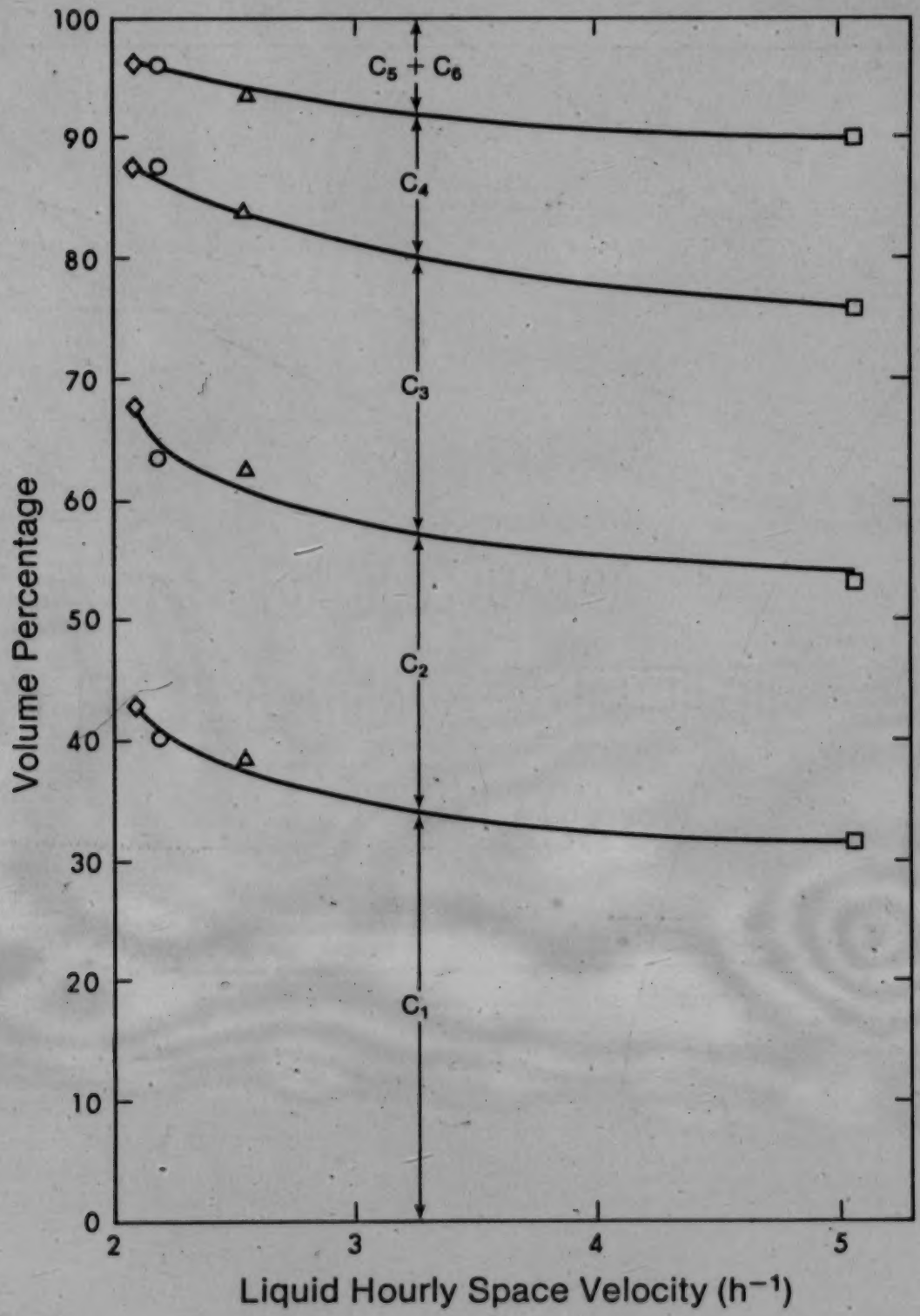


Figure 12: Effect of LHSV on the Composition of Gas Product at 13.8 MPa

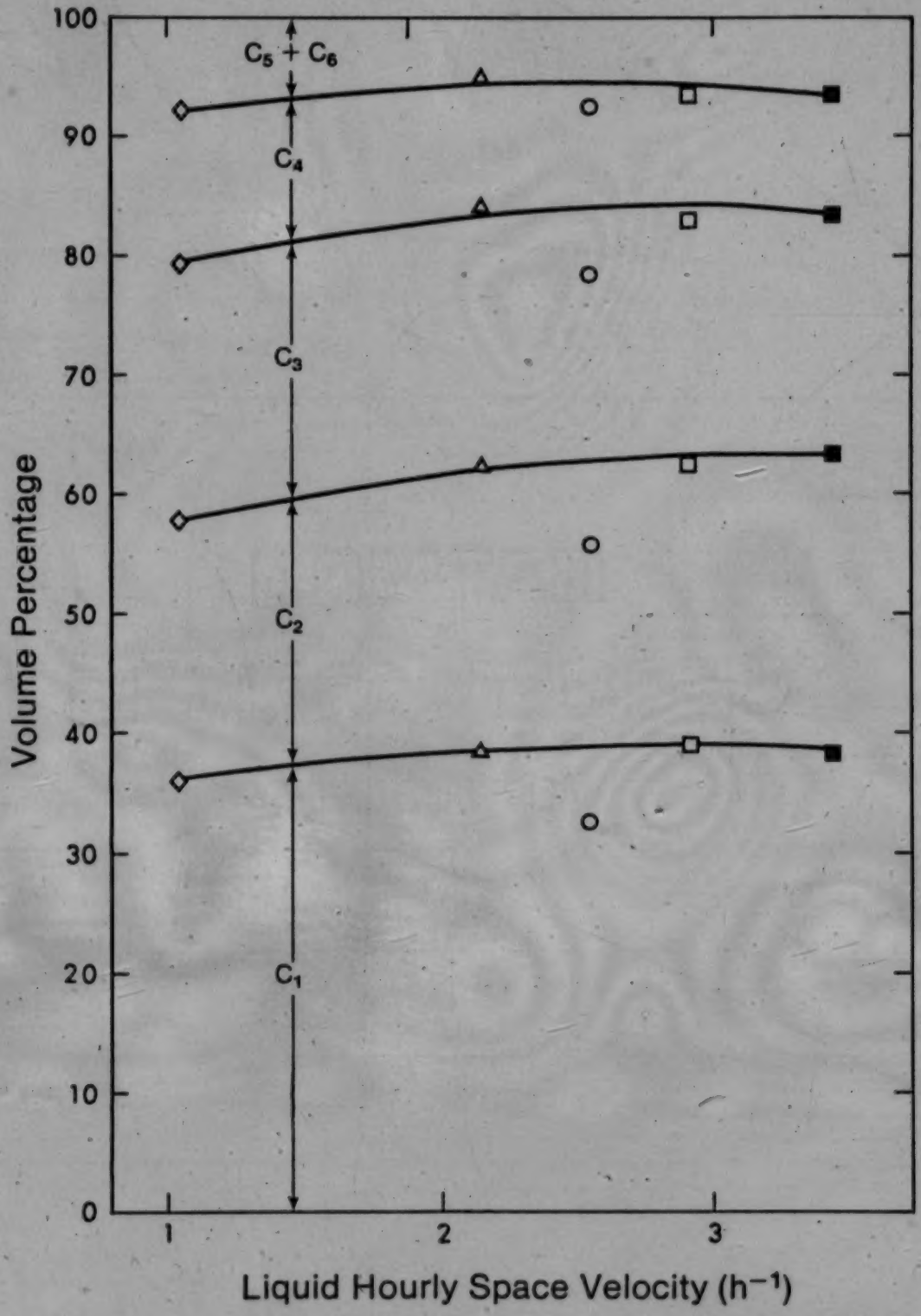


Figure 13: Effect of LHSV on the Composition of Gas Product at 17.2 MPa

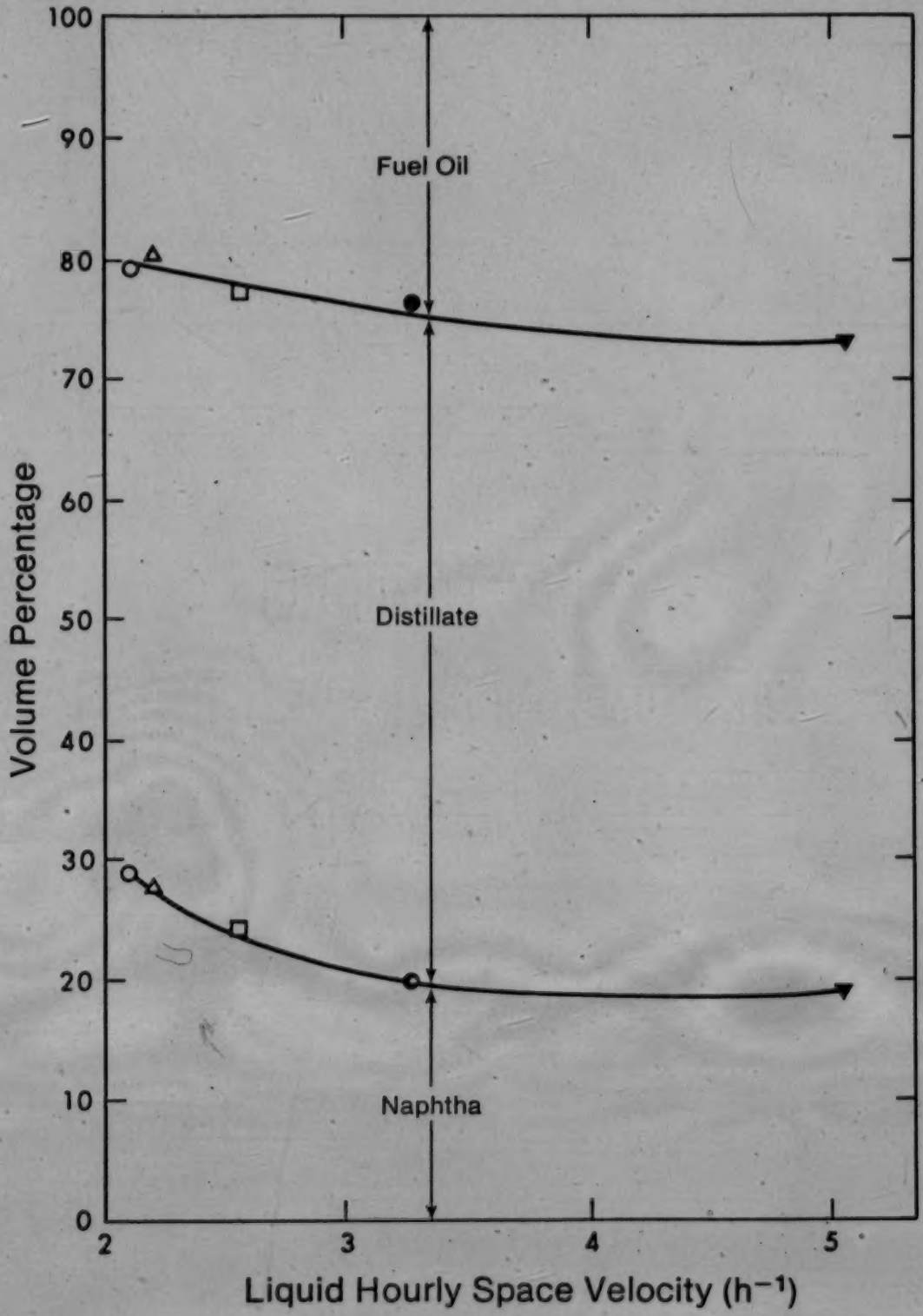


Figure 14: Effect of LHSV on the Composition of Liquid Product at 13.8 MPa

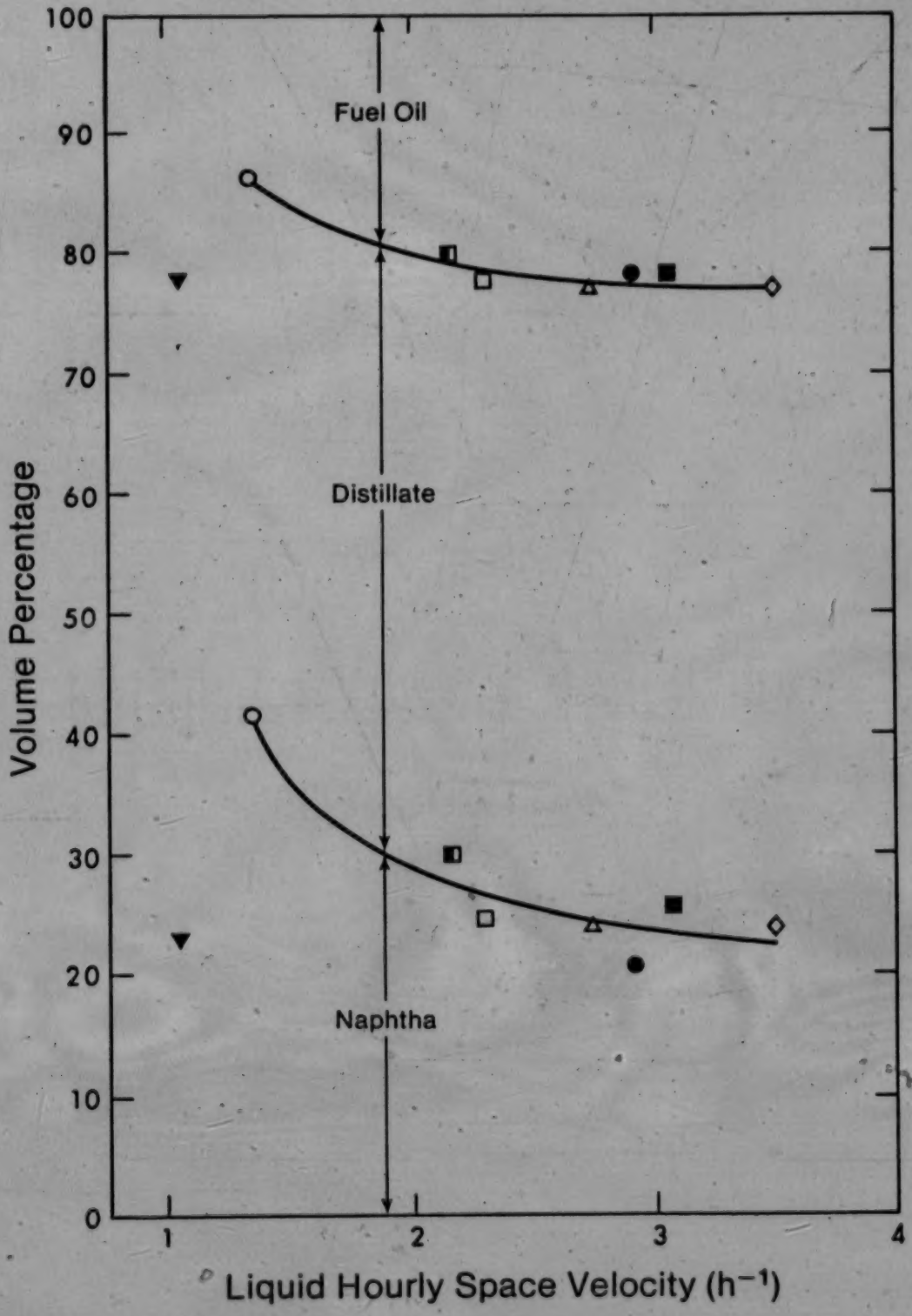


Figure 15: Effect of LHSV on the Composition of Liquid Product at 17.2 MPa

another indication of increasing hydrocracking as the LHSV decreased. Furthermore, it appeared that the fuel oil fraction was the main portion of the heavy gas oil being hydrocracked.

The effect of LHSV on the production of hydrocarbon gas product is shown in Figures 16 and 17. The flow rates of the gas product were calculated on the basis of unit volume flow rate of liquid feed, at a standard condition of 101.3 kPa and 15°C. More hydrocarbon gas product was produced as the LHSV decreased and as noted above the volume percent of lighter component such as methane, also increased with decreasing LHSV. The increase of hydrocarbon gas product rate with decreasing LHSV was more significant at a high pressure (17.2 MPa) than at a lower pressure (13.8 MPa).

C. Hydrocracking

Representing the rate of hydrocracking by

$$r_{HC} = - k_{HC} V \qquad (6.4)$$

where r_{HC} = rate of hydrocracking
k_{HC} = pseudo-reaction rate constant
V = volume % of fuel oil fraction

and assuming the reactor vessel to be constant stirred tank reactor (CSTR) leads to the following approximate

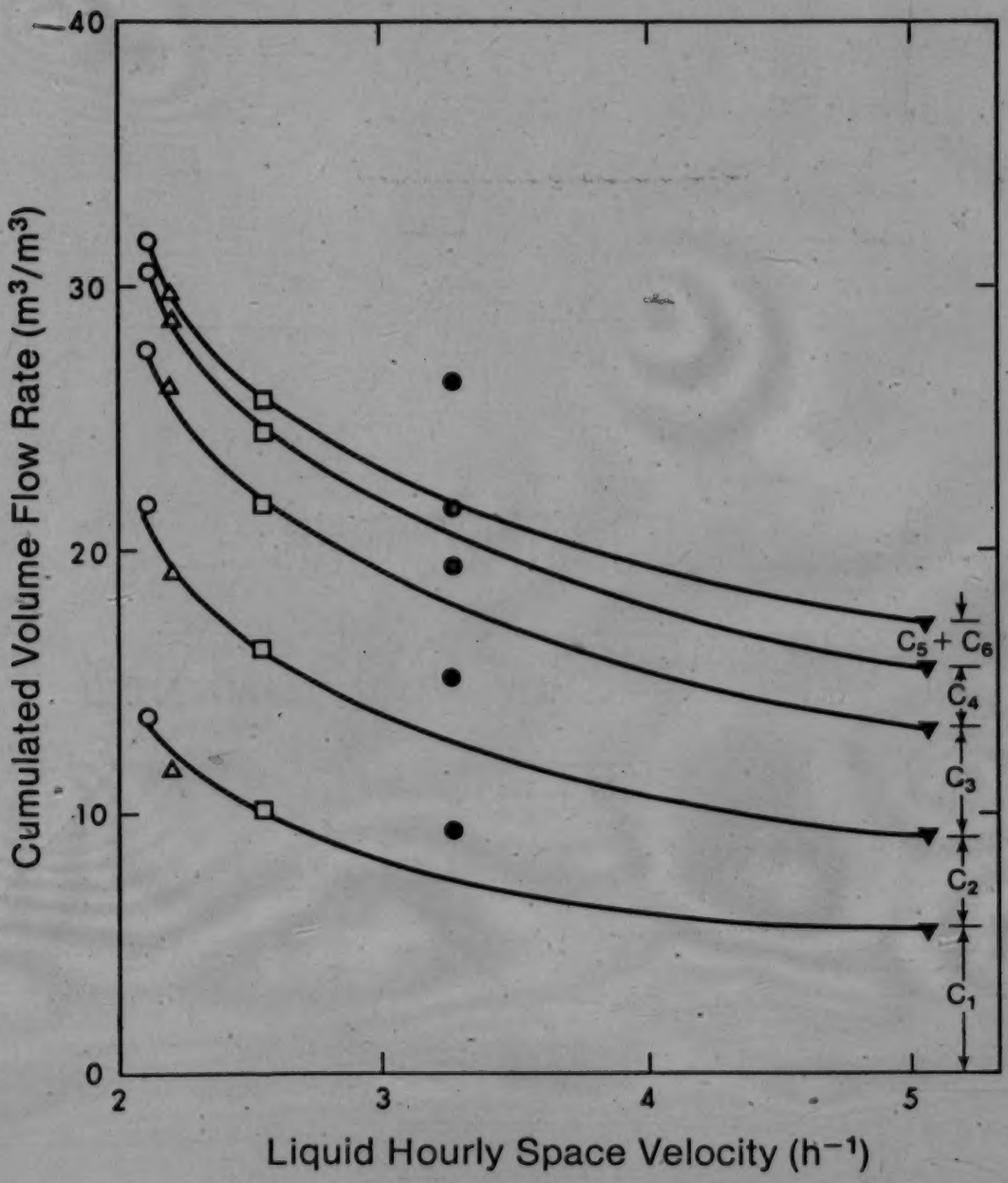


Figure 16: Effect of LHSV on Gaseous Product Rate at 13.8 MPa

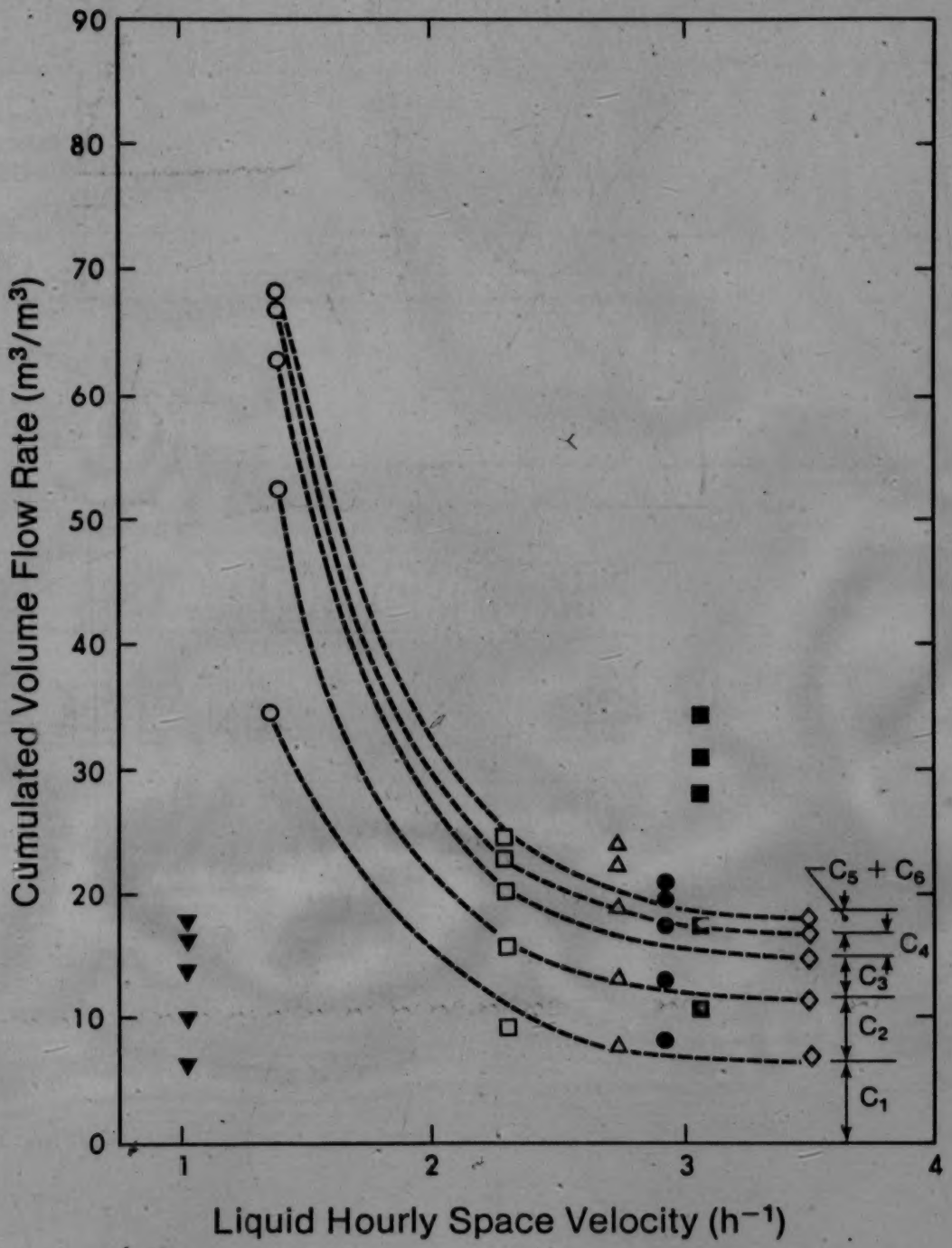


Figure 17: Effect of LHSV on Gaseous Product Rate at 17.2 MPa

relationship .

$$LH\ k_{HC}\ V_f = F_i\ V_i - F_f\ V_f \qquad (6.5)$$

where LH = liquid holdup volume in reactor

k_{HC} = reaction rate constant of hydrocracking

F_i, F_f = volumetric flow rate of liquid feed and liquid product respectively

V_i, V_f = volume % of fuel oil fraction in the liquid feed and the liquid product respectively

If, however, the effect of hydrocracking on volumetric flow rate of liquid feed and liquid product is negligible, then

$$F = F_i = F_f \qquad (6.6)$$

Equation (6.5) becomes

$$LH\ k_{HC}\ V_f = F\ (V_i - V_f) \qquad (6.7)$$

$$\frac{k_{HC}}{F/LH} = \frac{V_i - V_f}{V_f} \qquad (6.8)$$

$$\frac{k_{HC}}{LHSV} = \frac{V_i - V_f}{V_f} \qquad (6.9)$$

Figures 18 and 19 are plots of $V_i - V_f / V_f$ versus 1/LHSV, the slopes of which provide values of the pseudo first order rate constants, k_{HC}. The values obtained were 2.4 h^{-1} at 13.8 MPa and 450°C, and 2.8 h^{-1} at 17.2 MPa and 450°C. They were determined by means of a linear least

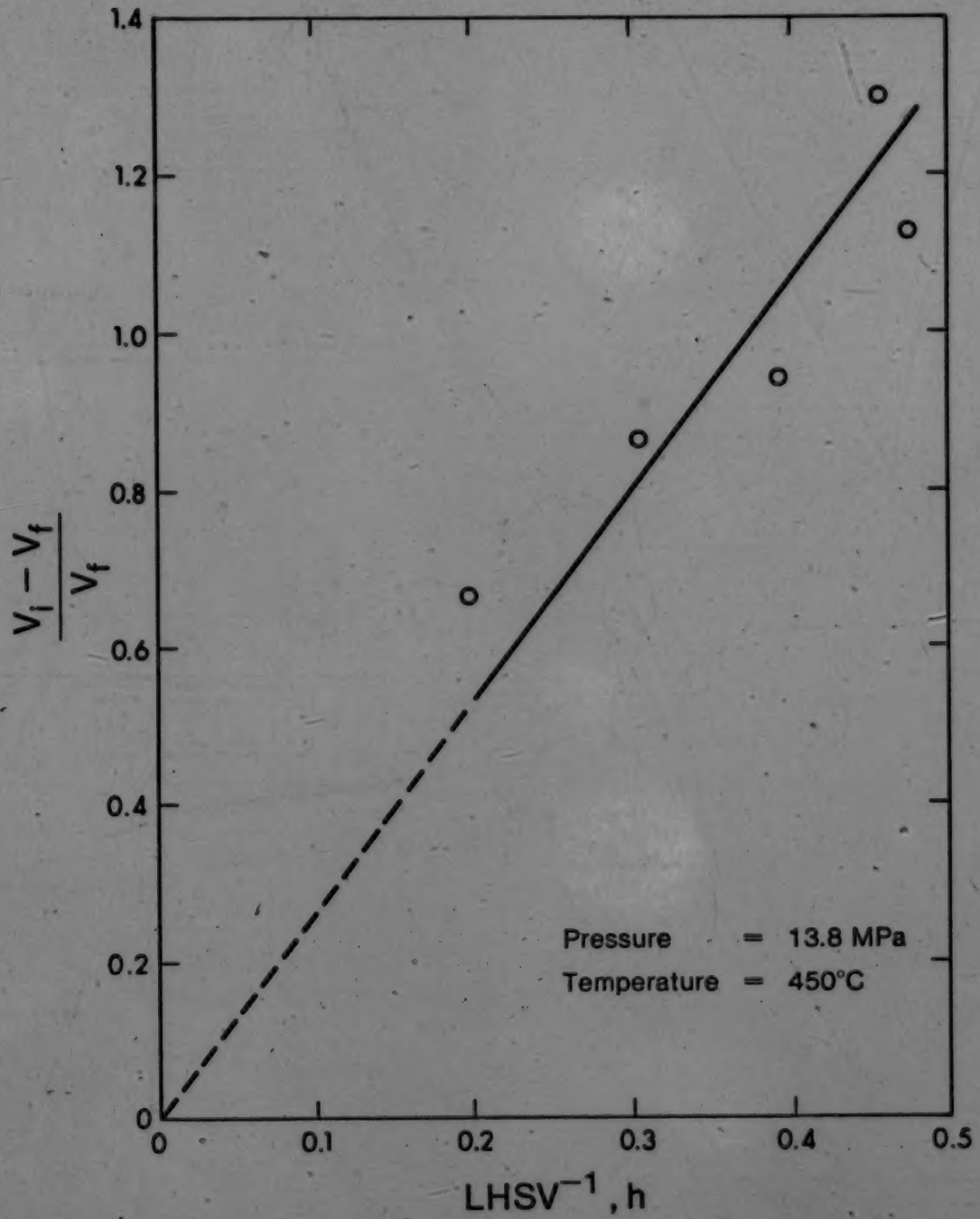


Figure 18: First Order Plot of Hydrocracking of the Fuel Oil Fraction in CANMET Heavy Gas Oil at 13.8 MPa

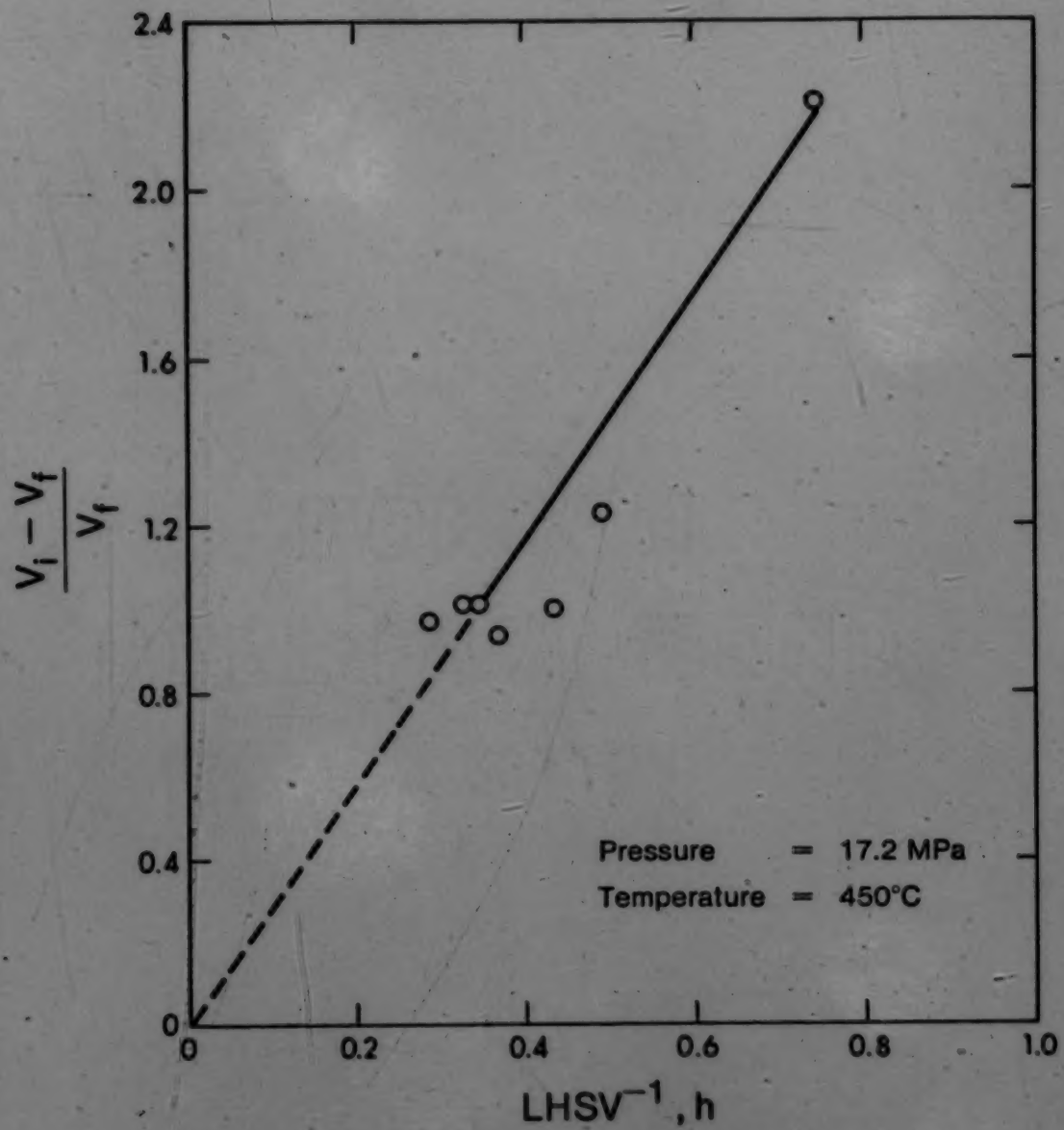


Figure 19: First Order Plot of Hydrocracking of the Fuel Oil Fraction in CANMET Heavy Gas Oil at 17.2 MPa

square fit of the data through the origin.

A plot of the ratio of the naphtha fraction to the distillate fraction, V_n/V_d, versus the naphtha fraction, V_n, is shown in Figures 20 and 21. The plot suggests that a linear relationship exists between V_n/V_d and V_n, that is

$$(V_n/V_d) = aV_n + b \qquad (6.10)$$

where V_n = volume % of naphtha fraction
V_d = volume % of distillate fraction
a,b = correlation constants

In this study, a and b were found to be 0.0225 and 0.0874, respectively, at 13.8 MPa, and 0.0263 and 0.0181 at 17.2 MPa.

This relationship implies that there is a sufficiently large reservoir of high boiling hydrocarbons (fuel oil fraction) to be drawn upon for hydrocracking. It is only valid within the operating ranges that the relationship is derived. This type of relationship is useful in predicting the composition of liquid product from hydrocracking.

A similar type of relationship was observed by Eqbal and Sarkar (5), and is shown in Figure 22. They studied the catalytic hydrocracking of a vacuum gas oil with a boiling range of 214 to 366°C +. The catalysts used were nickel-molybdate on a alumina support and uranium oxide impregnated on a commercial cobalt-molybdate on alumina

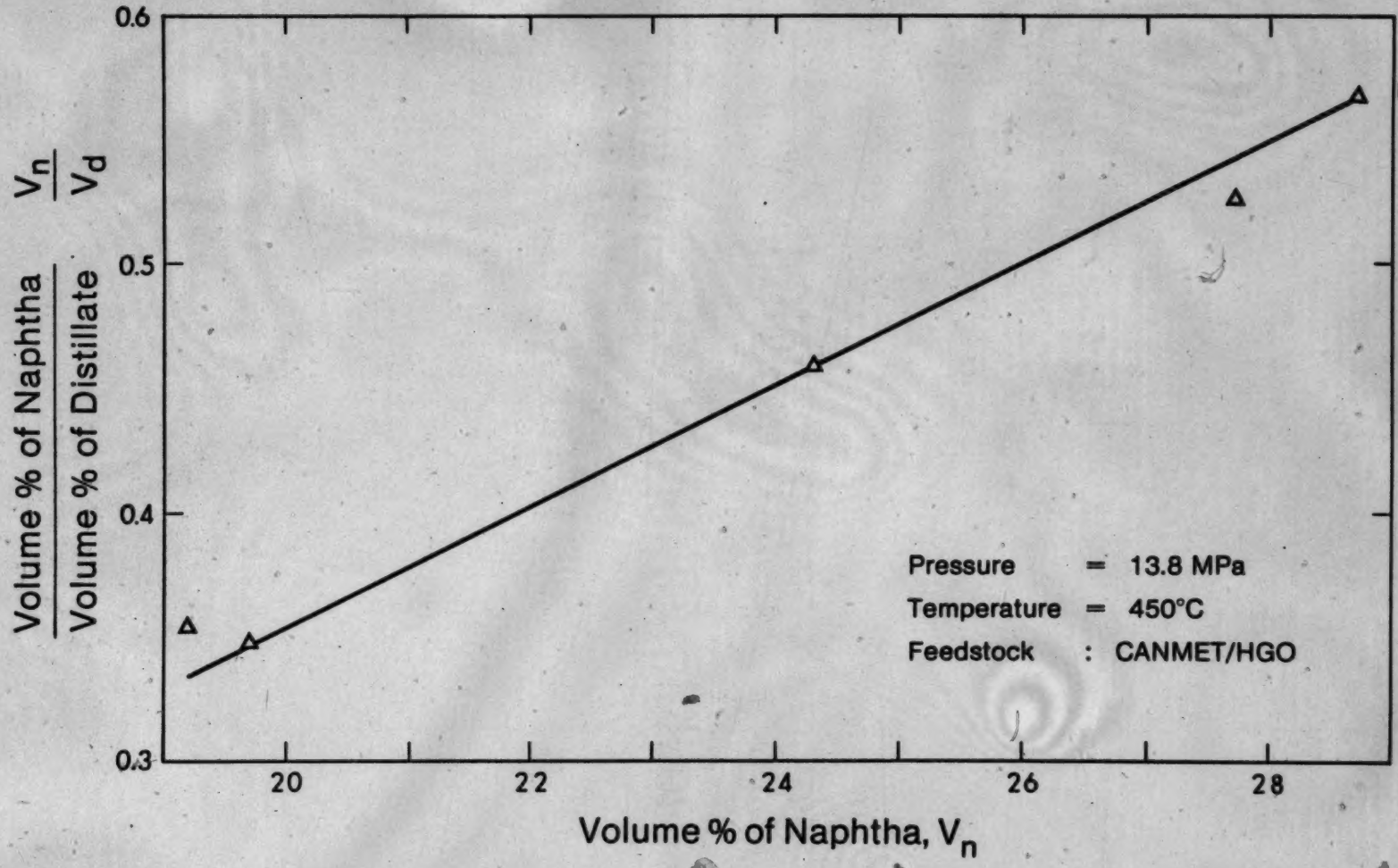


Figure 20: Effect of LHSV on the Liquid Product Distribution at 13.8 MPa

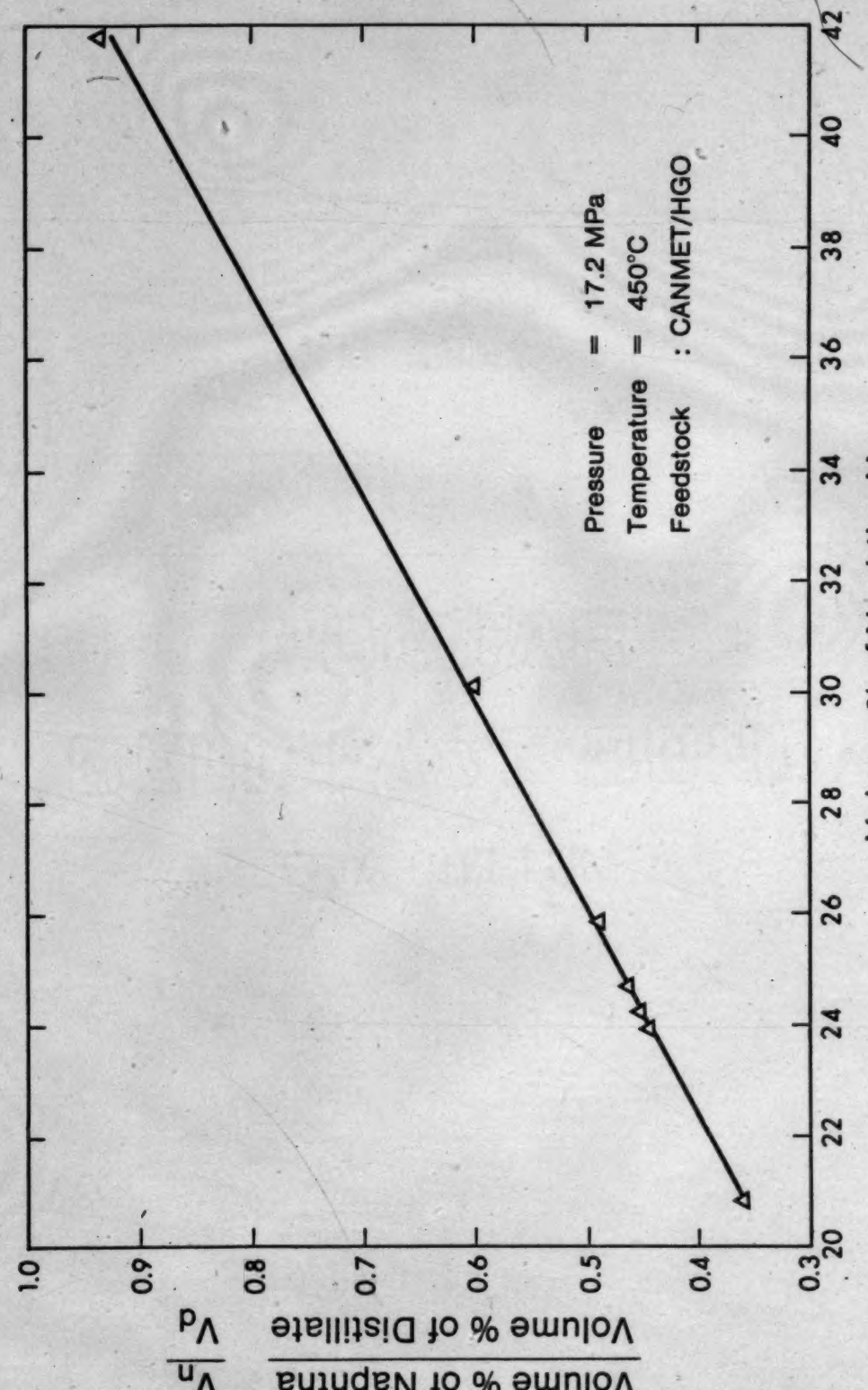


Figure 21: Effect of LHSV on the Liquid Product Distribution at 17.2 MPa

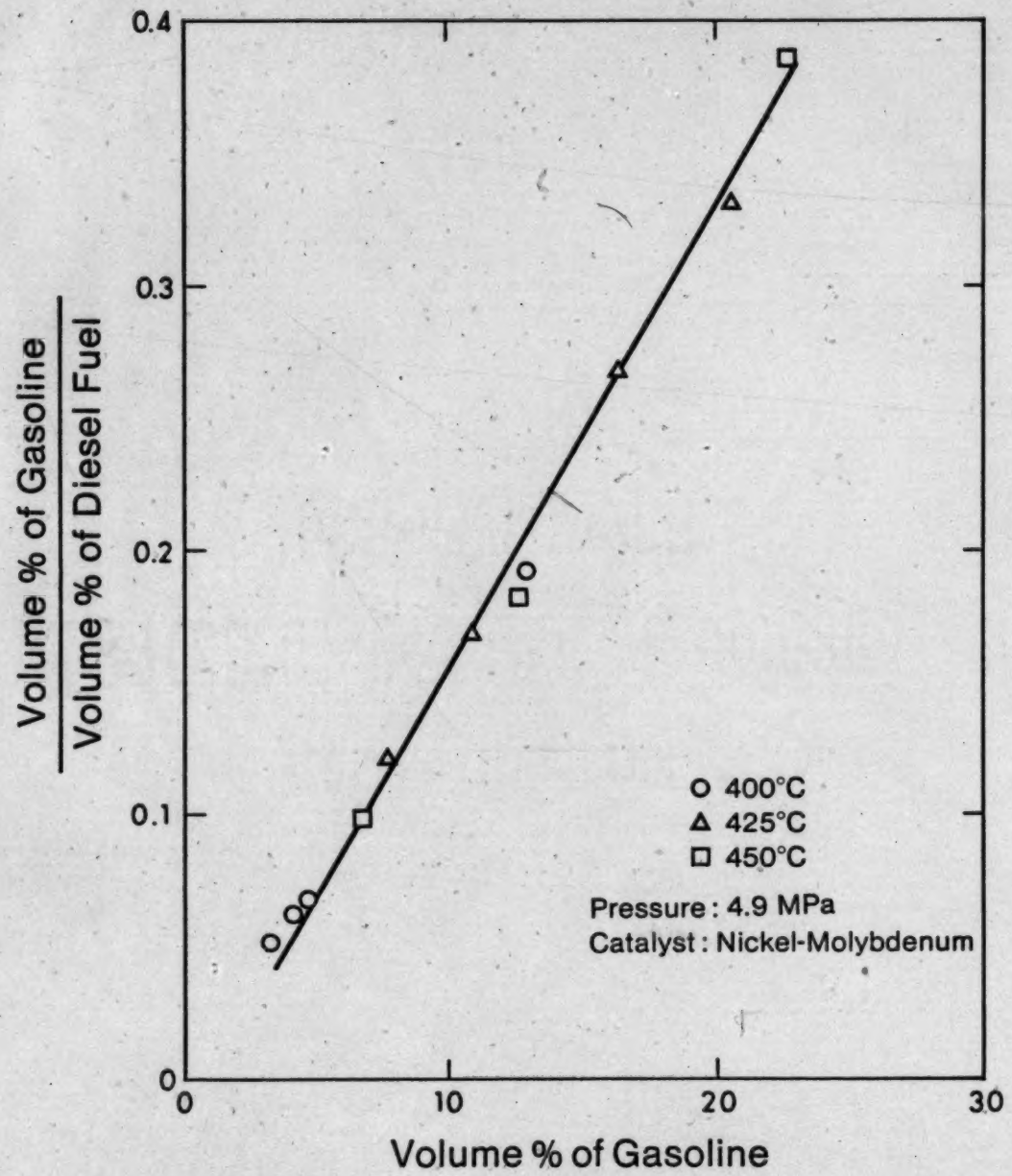


Figure 22: Hydrocracking of Vacuum Gas Oil (Eqbal and Sarkar)

support. The experiments were conducted in a continuous flow bench scale tubular reactor with a volume of 80 mL.

D. Hydrodesulfurization

An analysis similar to that for hydrocracking of the fuel oil fraction was performed to fit the data on sulfur depletion. Both first order and second order rate expressions were tried

$$\text{First Order: } r_{HDS} = - k_{HDS} S \qquad (6.10)$$

$$\text{Second Order: } r_{HDS} = - k_{HDS} S^2 \qquad (6.11)$$

where r_{HDS} = rate of HDS

k_{HDS} = rate constant of HDS, $wt.\%^{-1}h^{-1}$

S = sulfur content, wt.%

A better fit of the data was observed with the assumption of a second order rate expression.

Plots of $(S_i - S_f/S_f^2)$ versus (1/LHSV) are shown in Figures 23 and 24, where S_i and S_f are the sulfur content of the heavy gas oil entering and leaving the reactor. The pseudo second order rate constants were found to be 0.58 $wt.\%^{-1}h^{-1}$ and 0.65 $wt.\%^{-1}h^{-1}$, at 13.8 MPa and 17.2 MPa. The latter was valid for LHSV greater than 2.2. This result is comparable to other works (2, 20 and 14) which show that the reaction order of catalytic hydrodesulfurization varies between 1 and 2.

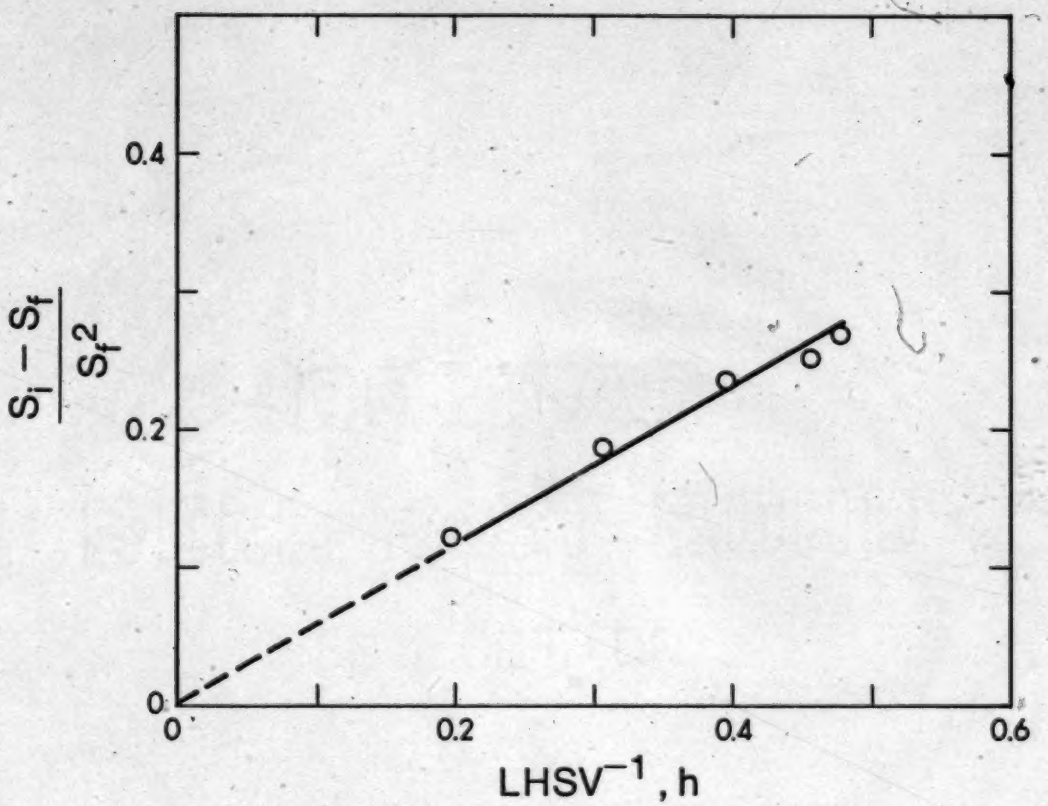


Figure 23: Second Order Plot of Sulfur Conversion at 13.8 MPa

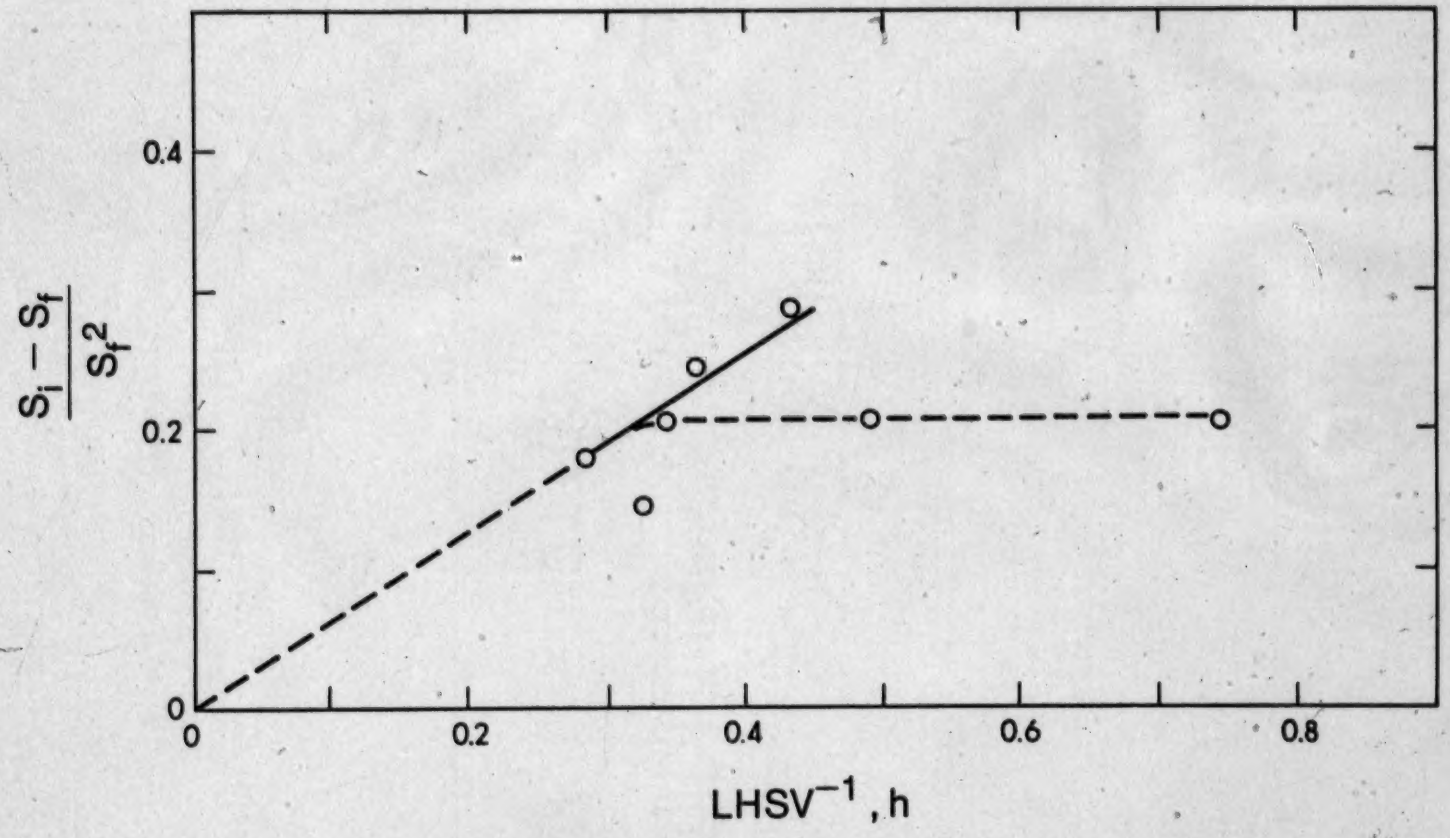


Figure 24: Second Order Plot of Sulfur Conversion at 17.2 MPa

At 17.2 MPa, when the operating LHSV was less than 2.2, the sulfur conversion appeared to stabilize at a nearly constant level (shown as broken line in Figure 24). One possible explanation is that the more reactive fraction of sulfur compound in HGO was depleted to a negligible level when the LHSV approached 2.2. The remaining sulfur compound was less reactive and did not follow second order rate expression.

E. Effect of LHSV on Hydrogen Consumption

Hydrogen consumption was calculated from the difference between the hydrogen feed rate and the hydrogen flow rate in the product gas stream. The former was measured prior to the start of a run when the reactor pressure was at the desired operating value and the temperature was at ambient level. The latter was measured during the run. The hydrogen consumption was reported as the amount of hydrogen consumed (at 15°C and 101.3 KPa) per unit volumetric liquid feed rate (at 15°C and 101.3 KPa).

Four Runs #9031, 9029, 9033 and 9036, the measured hydrogen consumptions were found to be negative. This implied that net hydrogen was generated. Since both hydrocracking and hydrodesulfurization were reactions that consumed hydrogen, therefore these four data points were suspected to be erroneous as a result of poor measurement of hydrogen feed and gas product flow rates. They were discarded from the analysis.

Figure 25 shows that hydrogen consumption increases with a decrease of LHSV. This is consistent with what one would expect to find at lower LHSV when the extent of hydrodesulfurization and hydrocracking increase.

F. Catalytic Hydroprocessing

The result of the catalytic hydroprocessing of CANMET HGO shows that an increase of reactor temperature leads to a decrease of specific gravity and sulfur content of the liquid product (See Table 8). The decrease of specific gravity corresponds to increased naphtha fraction and reduced fuel oil fraction. The naphtha fraction, which has a lower boiling point range, tends to have a lower specific gravity than the fuel oil fraction. In addition, the increase of reactor temperature also results in an increase in the amount of gas product. All these results are what one would expect to find with an increase of the extent of hydrocracking and hydrodesulfurization, which is directly associated with increasing reactor temperature.

Compared with thermal hydroprocessing (Run #9022) under similar operating condition, catalytic hydroprocessing (Run #9040) results in higher level of sulfur conversion and hydrocracking. The reduction of sulfur content is increased from 24.0% to 96.5%, while the reduction of fuel oil fraction (343°C+) is increased from 55.1% to 72.7%. Furthermore, the specific gravity and the bromine number of the liquid product also decrease with catalytic

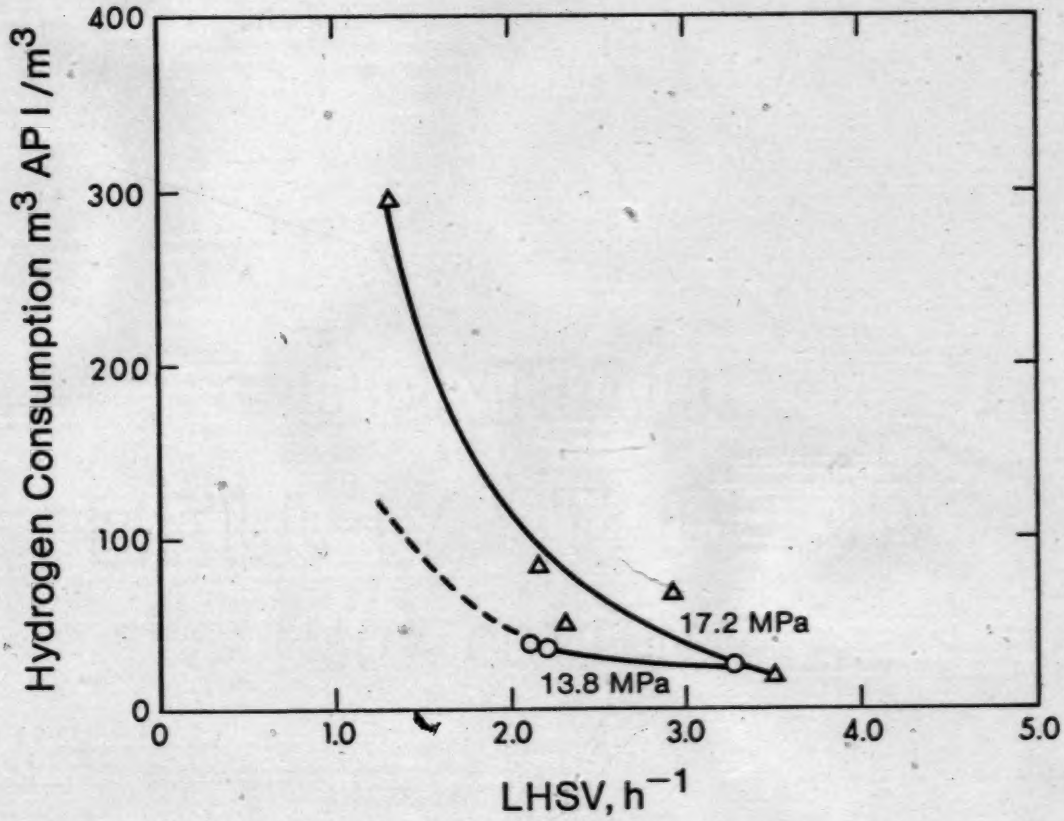


Figure 25: Hydrogen Consumption -- Hydrocracking of CANMET Heavy Gas Oil at 450°

hydroprocessing. The decrease of specific gravity of liquid product is the direct result of an increase of naphtha fraction from 5.6% to 39.4%, evidence of increased hydrocracking. The decrease of bromine number indicates that the presence of unsaturated hydrocarbon is reduced. This is primarily due to promotion of saturation reactions by the catalyst.

For the catalytic hydroprocessing, as in thermal hydroprocessing. LHSV is defined as the liquid hourly feed rate per unit volume of liquid holdup in the reactor. This definition is unsatisfactory as it does not take into account of the quantity of catalyst being used. An alternate definition will have to be developed in order to use the CSTR system in the kinetic study of catalytic hydroprocessing.

G. Material Balance

Material balance calculation carried out for each run. The balance was based on the average mass flow rates of the reactants, $\dot{M}_f$, and the products, $\dot{M}_p$.

The discrepancy of material balance, ε_m, was defined as the ratio of $(\dot{M}_f - \dot{M}_p)$ to $\dot{M}_f$, and was expressed on a percentage basis (See Appendix E.2).

For thermal hydroprocessing runs, ε_m was found to vary between ±4.5%. As for catalytic hydroprocessing runs, ε_m ranged from -5.8% to 5.5%, with the exception of Run #9038 (ε_m = 14.5%). The large discrepancy of that run was mainly

due to poor control on the hydrogen feed, resulting in a substantial drop of flow at the end of run as compared to the start of run.

VIII. RECOMMENDATIONS

This work indicates that the following changes can be made to improve the operation of the reactor system and the accuracy of data:

(1) Hydrogen Consumption

The present method of measuring the hydrogen consumption involves taking the difference between the hydrogen flow in the feed and product gas. The flow rates of feed and product gas are obtained by means of the same dry gas test meter. This method is unsatisfactory because of poor accuracy as the two flow rates cannot be measured simultaneously. The poor accuracy is demonstrated by the evidence that negative values are obtained in several runs which is contrary to the fact that both hydrocracking and hydrodesulfurization are reactions that consume hydrogen.

The method can be improved by the installation of mass flow meter that is capable of measuring low gas flow at high pressure. It is important that separate measuring elements be available for both the gas feed and the gas product streams.

(2) Hydrogen Sulfide Content in Product Gas

The existing gas chromatographic system for analyzing the product gas stream is unable to isolate and detect the hydrogen sulfide from the other

components. This makes it necessary to use an alternative method (absorption and titration) to measure the hydrogen sulfide content. The absorption/titration method is unsatisfactory because of the long analytical time. Furthermore, the accuracy of the absorption/titration method is inferior to the gas chromatography, because the caustic scrubbing solution will react not only with hydrogen sulfide, but also with carbon dioxide and mercaptans.

Since the presence of hydrogen sulfide in the product gas stream can be confirmed by the Absorption/Titration method. It is reasonable to assume that hydrogen sulfide has either been retained in the gas chromatographic columns or eluted out of the columns together with one of the other components. For the former case, improvement can be made by using an alternate valve switching sequence; whereas, for the latter, different column packing may be used to alleviate the problem.

IX. CONCLUSION

A continuous flow, stirred tank reactor system was used to study the hydrocracking and the hydrodesulfurization of a heavy gas oil derived from hydrocracked Athabasca bitumen. This oil has a boiling range of 132 to 491°C, a specific gravity of 0.915 and a sulfur content of 2.0%.

The results showed that a reasonable fit of data can be obtained by assuming a first order and a second order type of rate expression for the hydrocracking and the hydrodesulfurization, respectively

$$r_{HC} = - k_{HC} V$$

$$r_{HDS} = - k_{HDS} S^2$$

where r_{HC}, r_{HDS} = rate of HC and HDS

k_{HC}, k_{HDS} = reaction rate constants of HC and HDS

V = volume % of fuel oil fraction

S = sulfur content, weight %

In addition, the ratio of naphtha fraction to distillate fraction, V_n/V_d, was found to be directly proportional to the naphtha fraction, V_n.

It was also observed that at constant temperature and pressure, the extent of thermal hydrocracking and hydrodesulfurization, together with the hydrogen consumption, increased as the liquid hourly space velocity

decreased. In addition, at the same temperature, the hydrogen consumption increased and the hydrocarbon gas make decreased, with increasing reaction pressure.

This study has demonstrated that a small scale pilot unit can be used to provide useful information on hydroprocessing, such as rate data and hydrogen consumption, for scale-up purposes. In addition, operating procedures for the pilot unit and the related analytical techniques have been developed.

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APPENDIX A: EQUIPMENT DIAGRAMS

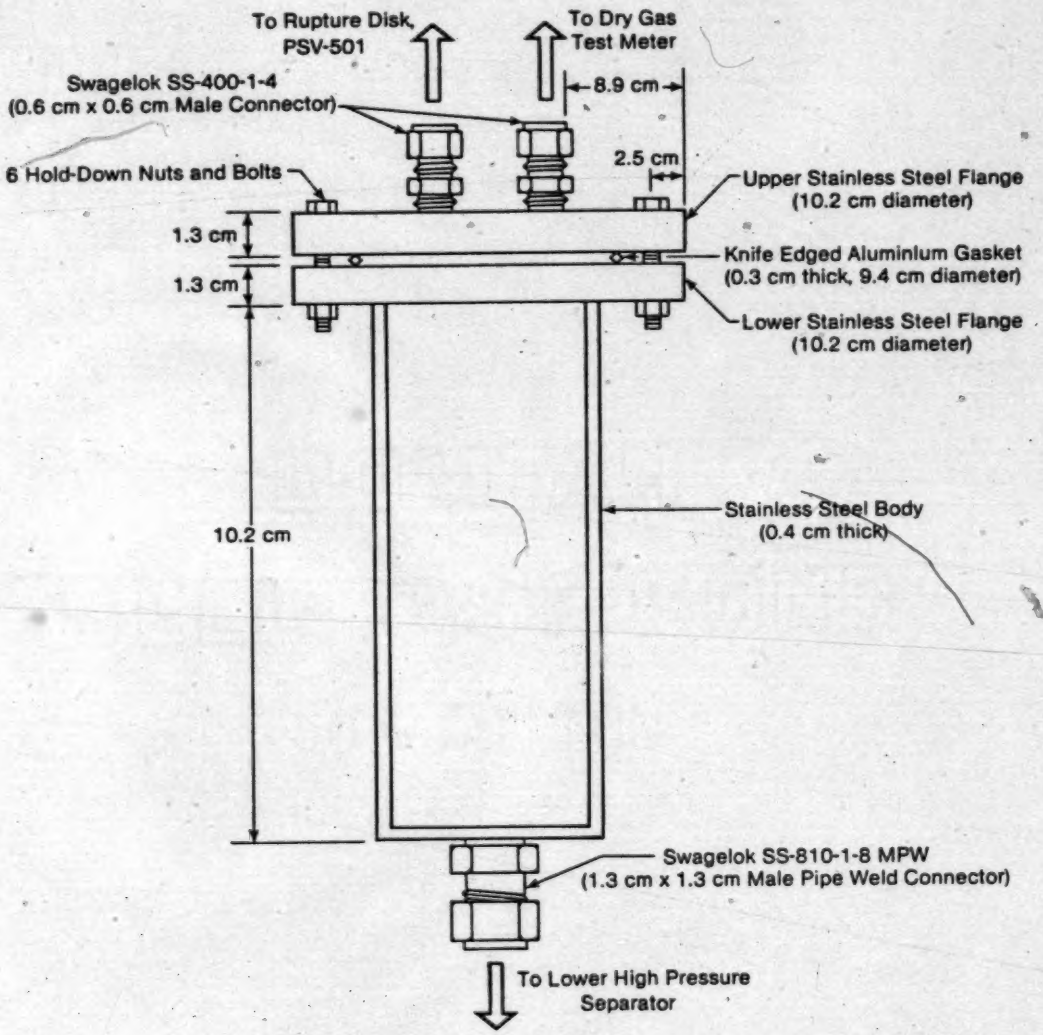

Figure A-1: Upper High Pressure Separator, S-1

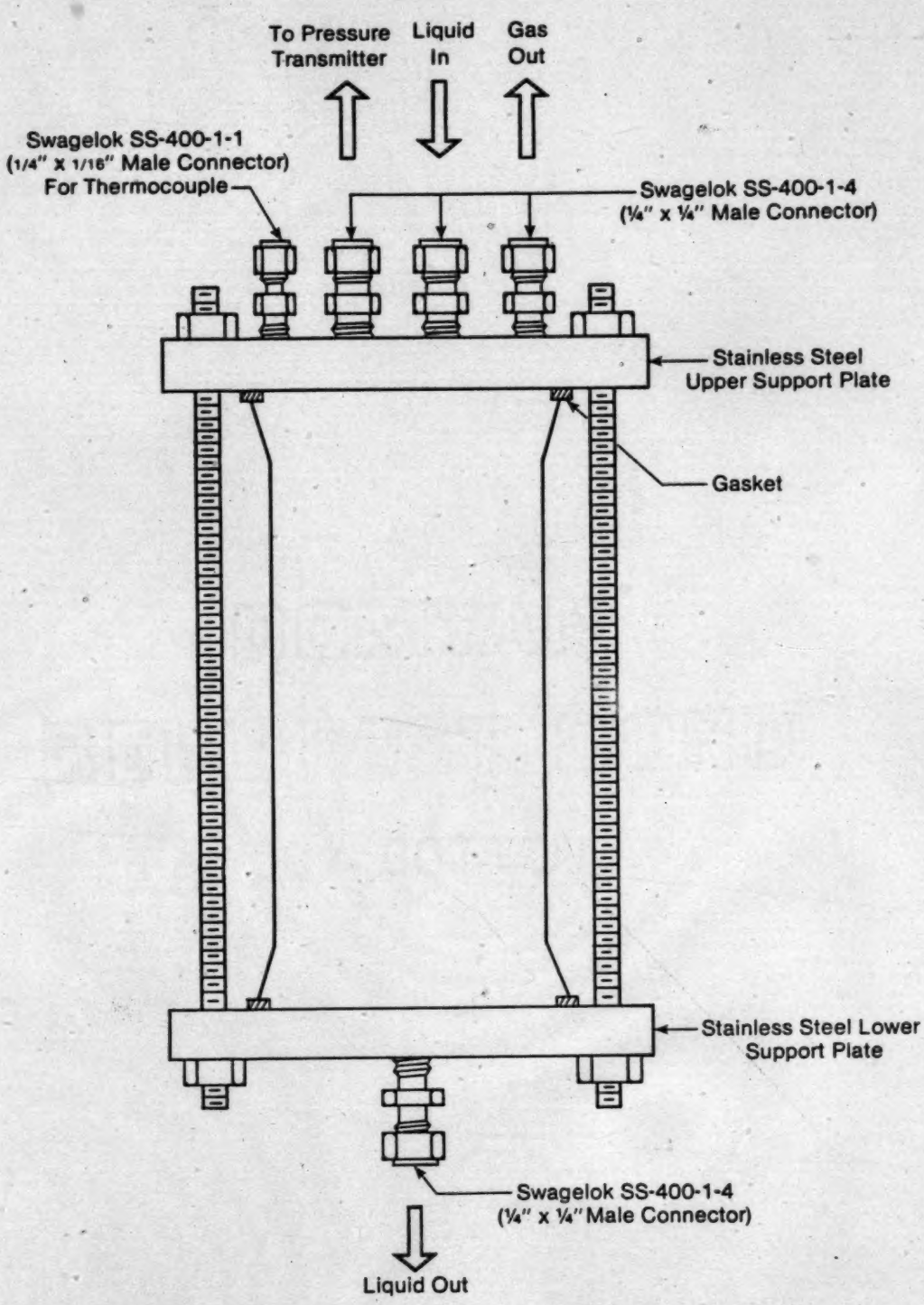

Figure A-2: Product Tank, S-3

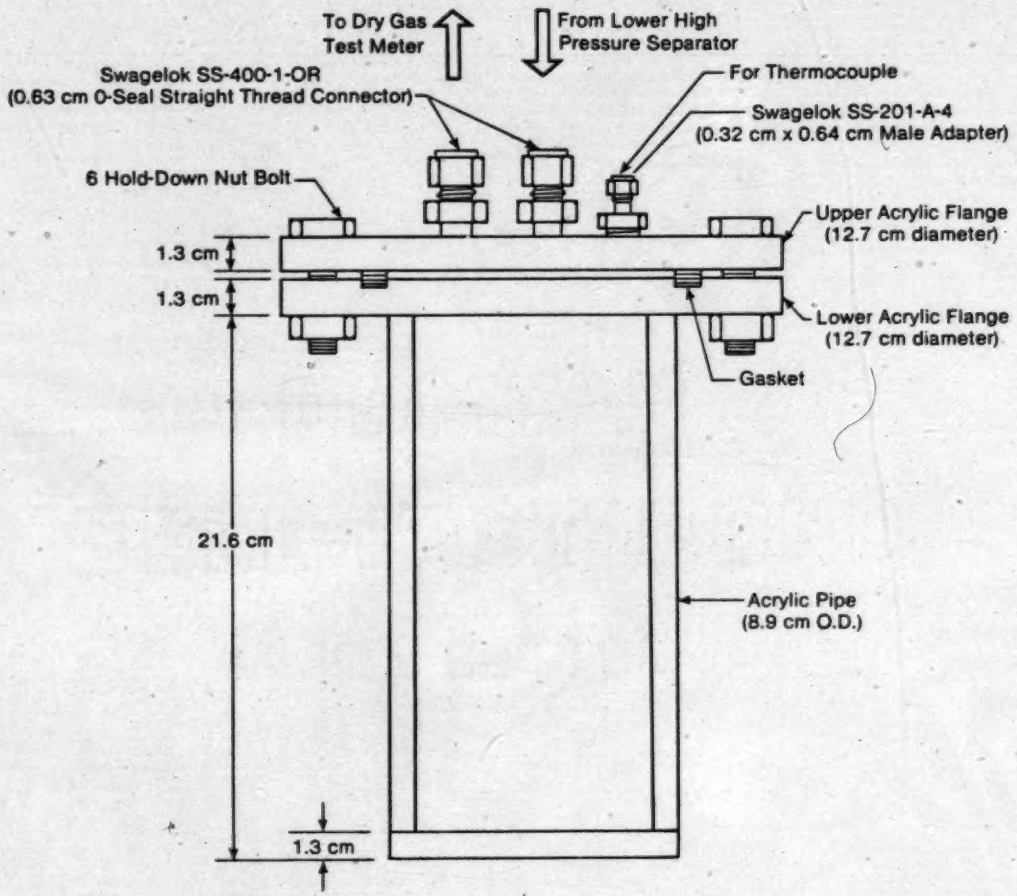

Figure A-3: Auxillary Product Tank, S-4

APPENDIX B: DETAILED OPERATING PROCEDURES

Operating Procedure

B.1 Startup Procedures

The routine startup procedures are listed as follows:

1. Turn on instrument air and power supply.
2. Check instrumentation, liquid feed pump and reactor, repair if necessary.
3. Check if there is sufficient hydrogen to last through the intended run; if not, replace depleted hydrogen cylinder with full ones.
4. Fill the liquid feed tank with the intended feedstock.
5. Fill the reactor with 120 mL of liquid feed.
6. Assemble the reactor as described in manufacturer's manual -- 'Operating and Maintenance Manual for Autoclave Engineers' Bolted Closure Packles Autoclave'
   a. Replace closure gasket.
   b. Replace cover assembly and MagneDrive.
   c. Hand screw the hex socket cap screws into the reactor body.
   d. Tighten each screw with a torque wrench (5.5 kgm for normal operating condition).
   e. Replace drive belt and belt guard.
   f. Replace stator.
7. Tighten up all loose connections.
8. Fill the lower high pressure separator, S-3, with 20 mL of liquid feed if it is empty, from the top of upper high pressure separator, S-2.

9. Fully open all manually operated valves, except the sampling valve, SV-601.
10. Set all controllers to "auto" mode.
11. Set all controller-setpoints to their respective operating values.
12. Set FC-101 to "manual" mode and close FCV-101.
13. Fully open hydrogen cylinder regulator valve.
14. Adjust PRV-101 until the downstream pressure of the valve is 0.14 MPa above the desired reactor pressure.
15. Slowly open FCV-101 via FC-101 until it is 5% open.
16. Close the hydrogen cylinder regulator valve when hydrogen passes through the Dry Gas Test Meter steadily.
17. Close FCV-101 via FC-101 until it is 100% closed.
18. Close the by-pass valve in hydrogen flow control loop 101.
19. Allow the unit to sit for half an hour.
20. The unit is considered to be leak free when the drop in the pressure of reactor and high pressure separators is less than 68.9 KPa in half an hour.
21. Repair leakage, if any, and check again until the unit is leak free.
22. Start the liquid feed pump, P-1.
23. Adjust the pump strokes of P-1 until the desired liquid feed rate is reached.
24. Fully open the by-pass valve in the hydrogen flow control loop 101.
25. Manually set the FCV-101 to be 5% open via FC-101.

26. Fully open the hydrogen cylinder regulator valve.
27. After the hydrogen flow has stablized, slowly close the by-pass valve in the hydrogen flow control loop 101.
28. Measure the flow rate of hydrogen leaving the unit with the Dry Gas Test Meter, after the pressure in R-1, S-1 and S-2 have reached their respective steady state operating conditions.
29. Adjust the opening of FCV-101 until the desired hydrogen flow rate is reached.
30. Adjust the setpoint of FC-101 so that it coincides with the input signal to the controller.
31. Switch FC-101 from "manual" to "auto".
32. Make minor adjustment on all controller-setpoints, if necessary until the desired operating conditions and feed rates are achieved.
33. Start cooling water circulation to the cooling jacket of the stirrer.
34. Start the agitator.
35. Adjust the rotation speed of the agitator until the desired value is reached.
36. Slowly bring the reactor temperature up to desired operating value at a rate of approximately 200°C per hour by raising the setpoint of TC-401.
37. After the system has stablized at the desired condition for two hours, direct the liquid product line leaving the lower high separator to product tank.

38. Switch the gas product line from auxiliary liquid product tank to liquid product tank.
39. Sampling begins when the unit has been running at the operating condition for over two hours.
40. The last liquid sample is taken when constant gas product analysis has been achieved.

B.2 Routine Shutdown Procedures

The routine shutdown procedures are listed as follows:

1. Close the hydrogen cylinder shutoff valve..
2. Change FCV-101 from "AUTO" to "MANUAL".
3. Fully open the by-pass valve in the hydrogen flow control loop 101.
4. Shut off simultaneously the feed pump and the valve on liquid product line leaving the reactor.
5. Shut off the liquid feed tank valve.
6. Reduce the setpoint of TC-401 to 0°C.
7. Direct the liquid product line from the product tank to auxiliary product tank.
8. Direct the gas product line from the product tank to auxiliary product tank.
9. Turn off the agitator, when the reactor temperature has reduced to 350°C.
10. Shut off Recorders 1 and 2.
11. Shut off cooling water to the stirrer.

B.3 Routine Presulfiding of Catalyst

1. Fill catalyst basket with the desired amount of catalyst.
2. Replace the top cover of catalyst basket.
3. Tighten up the hold-down bolts of the catalyst basket.
4. Fill the reactor with 120 mL of liquid feed.
5. Assemble the reactor as described in the manufacturer's manual -- "Operating and Maintenance Manual for Autoclave Engineers' Bolted Closure Packless Autoclave"
   a. Replace closure gasket.
   b. Replace cover assembly and MagneDrive.
   c. Hand screw the hex socket cap screws into the body.
   d. Tighten each screw with a torque wrench.
   e. Replace drive belt and belt guard.
   f. Replace stator.
6. Tighten up all loosen connections.
7. Flush the reactor system with hydrogen.
8. Manually close FCV-101 and PCV-405.
9. Fully open hydrogen cylinder valve.
10. Slowly open FCV-101 until it 25% open.
11. Shut off FCV-101 as soon as the reactor pressure has reached 13.8 MPa (2000 psig).
12. Close hydrogen cylinder valve.
13. Close by-pass valve on hydrogen flow loop 101.
14. Gradually raise the setpoint of TC-401 until the reactor temperature has reached 420°C.
15. Maintain the reactor temperature at 420°C for two hours.

16. Prepare 150 mL of liquid feed which contains 2% by volume of carbon disulfide.
17. Fill the liquid feed tank with liquid feed containing carbon disulfide.
18. Lower reactor temperature to 350°C.
19. Open the liquid feed tank valve.
20. Start the liquid feed pump.
21. Adjust the pump setting until it is delivering 1 mL/min.
22. Set PC-405 to 13.8 MPa (2000 psig).
23. Set PC-501 to 2.4 MPa (350 psig).
24. Open the hydrogen cylinder valve.
25. Slowly open FCV-101 until it is 10% open.
26. Adjust FCV-101 so that a flow rate of 0.350 L/min of gas product is measured with Dry Gas Test Meter.
27. Slowly raise the reactor temperature to 400°C.
28. Adjust the setpoint of FC-101 to coincide with the input signal.
29. Maintain the same operating conditions for two hours.
30. Switch the liquid feed line from feed tank to burette.
31. Replace the carbon disulfide-containing liquid feed with pure liquid feed.
32. Switch the liquid feed line from burette to feed tank.
33. Maintain the same operating conditions for three hours.
34. Shut down the unit, following the routine shutdown procedures.

APPENDIX C: ANALYTICAL PROCEDURES

C.1 Principle of Simulated Distillation Analysis (SDA)

The simulated distillation of petroleum fractions by gas chromatography works on the principle that individual components of a petroleum sample elute from gas chromatographic columns in the order of increasing boiling points. A column packing containing a non-polar stationary phase, such as Dexsil 300 GC on Chromsorb W, is preferred because it has a limited efficiency and resolution, both of which minimize the discriminating effect of packing on separation according to different classes of hydrocarbon.

A linear relationship exists between the boiling point of n-paraffins eluting from gas chromatographic columns and their corresponding retention time. This relationship is specific for each pair of gas chromatographic columns and the operating condition of the gas chromatograph being used. It is obtained by running a calibration standard that contains a series of n-paraffins. N-paraffins are chosen because they are readily available commercially in high purity.

$$(BP)_t = Ks(RT)_t \qquad (C.1.1)$$

where $(BP)_t$ = boiling point

$(RT)_t$ = retention time

Ks = proportionality constant

By assuming the response factors of all hydrocarbon to be the same, the cumulative area under the chromatogram will be directly proportional to the cumulative amount of sample

eluted from the chromatographic column.

$$V_i = kA_i \qquad (C.1.2)$$

$$V_T = kA_T \qquad (C.1.3)$$

$$V = V_i/V_T \times 100\% = A_i/A_T \times 100\% \qquad (C.1.4)$$

where V_i, A_i = the cumulative volume of sample eluted from the column and the cumulative area under the chromatogram, at retention time (RT) of i

V_T, A_T = total volume of sample eluted from the column and total area under the chromatogram

V = volume % of sample eluted from the column at RT of i=t

k = proportionality constant

Combining the volume percentage of sample eluting from the column with the corresponding boiling point, a simulated distillation analysis (SDA) is obtained.

Because of the large number of theoretical stages available in a gas chromatographic column, the simulated distillation analysis provides a good approximation of the true boiling point distillation (TBP). This has been demonstrated by Green (8) and Eggertsen (4). In addition, Figures C.1 and C.2 show the difference between SDA and TBP obtained by means of Nester/Faust spinning band distillation column for Imperial Oil HAGO and CANMET heavy gas oil. The discrepancy between the two methods is within analytical error (±2%).

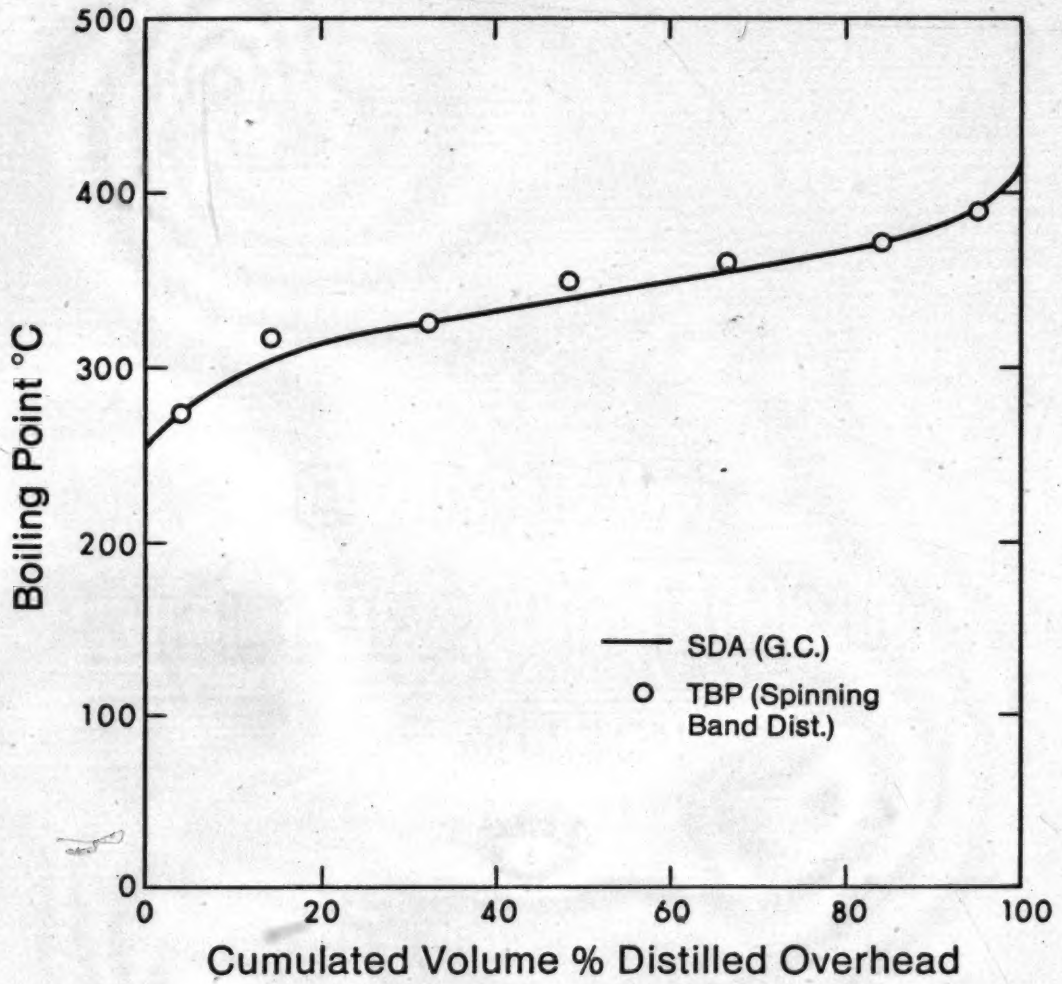

Figure C-1: Comparison of SDA and TBP for Imperial Oil HAGO

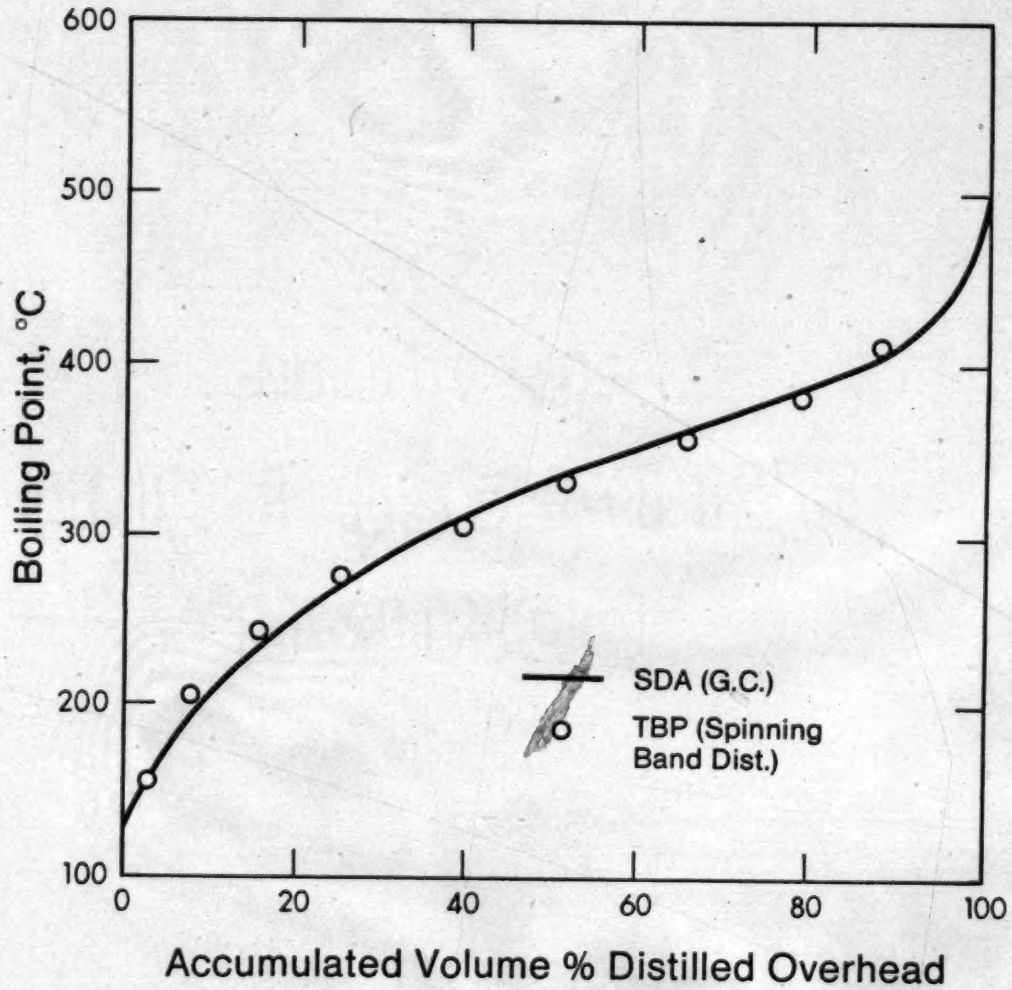

Figure C-2: Comparison of SDA and TBP for CANMET HGO

C.2 Analytical Procedures of Simulation Distillation Analysis

C.2.1 Conditioning of New Columns in HP5730A

1. Install the new analytical and reference columns.
2. Disconnect the detector end of the columns, so that the material eluting during conditioning does not enter the detector.
3. Move the LINE switch lever to the ON position.
4. Fully open the main valve of the carrier gas (helium) cylinder.
5. Adjust the regulating valve of the helium cylinder to a downstream pressure of 640 KPa.
6. Gently adjust the carrier gas flow control valves so that the flow rate of helium through the columns, measured with a soap film flowmeter is maintained at 50 ± 2 mL/min.
7. Set the temperature controls for the detector and injection port as follows:

   DETECTOR TEMP. : 350°C

   INJECTION TEMP. : 350°C

8. Set the following detector control slide switches:

   POLARITY : A

   SENSITIVITY : OFF

   OFFSET : NONE

   ATTENUATION : infinity

9. When the detector and injection port temperatures equilibrate, set the column oven programmer slide

switches as follows:

TEMP 1	:	360°C
TIME 1	:	0 min
TEMP 2	:	360°C
TIME 2	:	0 min
RATE	:	8°C/min

10. Press the SET NEW TEMP 1 button; the door will open and close immediately.
11. Leave the oven temperature at 360°C and the helium flowing through the columns for 24 hours.
12. After heating the columns at 360°C for 24 hours, reset TEMP 1 to 40°C and press the SET NEW TEMP1 button.
13. When the oven has cooled down to ambient temperature, reconnect the detector end of the two columns.
14. Cap the venting exit outlets of columns A and B with plugs.
15. Wait five minutes and note the carrier gas rotameters.
16. The system is considered leak tight if the rotameters indicate no flow.
17. If a leakage is detected, it has to be located with SNOOP and eliminated before proceeding any further.
18. Slowly remove the plugs from the venting exit outlets of columns A and B.
19. Adjust the helium flowrate, if necessary, to 50 ± 2 mL/min.
20. Set the ATTENUATION to 1 and SENSITIVITY to 5.

21. Enter the following setpoints into HP580A terminal via the keyboard:

ATTENUATION	:	1
ZERO	:	15.0
SLOPE SENSITIVITY	:	0
CHART SPEED	:	0.5 cm/min
AREA OF REJECTION	:	0.0
AUXILLARY SIGNAL	:	A

22. Then enter the time programming into the terminal as follows:

0.00	ZERO	15.0
0.01	INF	0
0.02	INF	4
0.03	INF	8
0.04	INF	9
0.02	INF	6
38.02	STOP	

23. Check whether the conditioning of the columns is completed or not by a blank or baseline run.
24. Press the START button when the READY light of HP5730A is on, and immediately following, press also the START button on the HP5840A terminal.
25. The chromatogram of the baseline run should be a stable line, without any fluctuation; if not, repeat Steps 2 to 21.
26. When a stable baseline chromatogram is obtained, check that every slice area underneath the chromatogram is

equal to or above zero; if yes, POLARITY setting remains to be A, otherwise, change the setting to B and repeat Steps 21 to 22.

27. New G.C. columns have to be used when an unstable baseline chromatogram or negative slice area appears consistently; repeat Steps 1 to 23 for the new columns.

C.2.2 Typical Daily Startup of HP5730A

1. Ensure the following switch settings on HP5730A are in place:

SENSITIVITY	:	5
OFFSET	:	NONE
ATTENUATION	:	1
DETECTOR TEMP.	:	350°C
INJECTION TEMP.	:	350°C
TEMP 1	:	40°C
TIME 1	:	0 min
TEMP 2	:	350°C
TIME 2	:	0 min
RATE	:	8°C/min

2. Set the POLARITY switch to A or B, depending on the finding during column conditioning, which gives upscale peaks.
3. Check whether the injection ports are leaking or not, using SNOOP; if not, proceed to Step 5.
4. If the injection parts are found to be leaking, tighten up the remaining nuts and check for leakage again,

repeat until no leakage is detected; replace the septums, if necessary.

5. When the detector and injection port temperatures have equilibrated, turn the OVEN MODE from OPEN to OPERATE.
6. Enter the following time programming into the HP5840A terminal:

0.00	ZERO	15.0
0.01	INF	0
0.02	INF	4
0.03	INF	8
0.04	INF	9
1.02	INF	6
38.02	STOP	

7. Next, enter the following:

SLOPE SENSITIVITY	:	0.1
AREA OF REJECTION	:	0
ATTENUATION	:	1
CHART SPEED	:	0.5 cm/min

8. Condition the columns by a blank or baseline run:
   a. Enter the run I.D. number.
   b. When the READY light is on, indicating that the column oven has reached temperature equilibrium, press the START button, and immediately following...
   c. Press the START button on HP5840A terminal to start the recording and integration.
9. The baseline chromatogram obtained should be a stable line and display no fluctuation; if not, repeat Step 8.

10. When a stable baseline is obtained, the HP5730A is ready for routine simulated distillation analysis.

C.2.3 Simulated Distillation Analysis of Light Petroleum Products

1. When the daily conditioning of the columns is completed, check and ensure the switch settings remain the same as stated in the TYPICAL DAILY STARTUP procedure.
2. Check for helium flow through the columns with a soap film flowmeter, if the flow rate remains 50±2 ml/min, proceed to Step 4.
3. If the helium flow changes, adjust accordingly and make a baseline run, then repeat Step 2.
4. Start a calibration run:
   a. Delete the existing time programming in HP5840A terminal and enter the following instead:

      0.00 ZERO 15.0

      38.01 STOP

   b. In addition, also enter:

      SLOPE SENSITIVITY : 0

      AREA OF REJECTION : 50

      ATTENUATION : 1

      CHART SPEED : 0.5 cm/min

   c. Finally, enter the identification number for the calibration run.
   d. Check and ensure the calibration mixture prepared in

advance in a capped vial, is in liquid state; heat it if necessary.

e. When the READY light is on, inject 1 uL of the liquid calibration mixture with a G.C. syringe into the injection port A and immediately...

f. Press the START button on the OVEN TEMPERATURE PROGRAMMER panel, then as soon as possible...

g. Press the START button on the HP5840A terminal to begin the recording and the integration.

5. Use the chromatographic result of the calibration run as input data to STAND which correlates the retention time and the boiling point by a linear least square fit.

6. The parameters of the correlation found, A0 and A1, are stored for later use.

7. Delete the existing time programming in the HP5840A terminal and enter the following instead:

0.00	ZERO	15.0
0.01	INF	0
0.02	INF	4
0.03	INF	8
0.04	INF	9
1.02	INF	6
38.02	STOP	

8. Start a baseline run:

a. Enter the I.D. number for the baseline run.

b. When the READY light is on, press the START button and immediately following...

c. Press the START button on HP5840A terminal.

9. The baseline chromatogram obtained should be a stable line and display no fluctuation; if not, repeat Step 8.
10. The chromatographic result of the baseline run is stored for future use.
11. Start a simulated distillation run of the sample to be analyzed:
    a. Enter the I.D. number for the sample run.
    b. When the READY light is on, inject 1 uL of the liquid sample with G.C. syringe into injection port A and immediately ...
    c. Press the START button on the OVEN TEMPERATURE PROGRAMMER panel, then as soon as possible ...
    d. Press the START button on the HP5840A terminal.
12. The chromatographic result of the sample run is used in conjunction with that of the baseline run and the correlation parameters obtained previously in Step 5, as input data to NEWS1 which converts the chromatographic results into simulated distillation result.
13. Repeat Step 11 for the next sample.

C.2.4 Typical Daily Shutdown

1. Reset the following switch settings:

ATTENUATION	:	infinity
SENSITIVITY	:	OFF

2. Leave the carrier gas (helium) following through the columns.
3. Leave the temperature settings on for the detector and the injection port.

C.3 Refinery Gas Analysis

Gas samples may be analyzed by using the Refinery Gas Analysis system. The system is installed in a Hewett-Packard Model 5840A gas chromatograph.

The gas chromatographic columns used are:

1. Reference columns
   a. 0.51 m of 10% UCW-892 silicone on 80/100 mesh chromsorb W-HP
2. Analytical Columns
   a. 7.32 m of 16% bis-2-methoxyethyl adiapate on 80/100 mesh P-AW and 1.52 m of 30% DC 200 silicone oil on 80/100 mesh chromsorb P-AW
   b. 1.83 m of Porapak Q, 80/100 mesh
   c. 3.04 m of molecular sieve 5A, 60/80 mesh

To accomplish the desired eluting sequence of components eluting from the chromotographic column, the following valves are used:

1. Two 6-port and one 10-port switching valves
2. Two Nupro needle valves.

C.3.1 Typical Daily Startup of HP5840A

1. Start up the gas chromatograph as recommended by the manufacturer.
2. Ensure the carrier gas used is a 8.5% hydrogen in helium mixture.
3. Adjust the flow rates of carrier gas through the chromatographic columns to 30±1 mL/min.
4. Ensure the following gas chromatographic settings are in place:

SLOPE SENSITIVITY	:	0.6
ATTENUATION	:	6
DETECTOR TEMP	:	100°C
INJECTION TEMP	:	100°C
TEMP 1	:	60°C
TIME 1	:	100
TCD SIGNAL	:	+B
CHART SPEED	:	0.5
AREA REJ	:	0

5. Turn on the TCD.
6. Allow the system to stablize which usually takes two to three hours.
7. Balance the TCD detectors as recommended by the manufacturers.
8. Adjust the two Nupro valves until the baseline shift due to valve switching is negligible, while the carrier gas flow remains at 30±1 ml/min.
9. The system is ready for a calibration run.

C.3.2 Calibration Run

1. Connect the standard gas mixture cylinder to the sampling line.
2. Crack open the cylinder valve.
3. Enter the following time programming steps:

   VALVE/EXT 3

   TIME 0.1

4. Adjust the sample flow control valve until a steady flow of standard gas mixture is passing through the gas chromatographic columns.
5. After maintaining the flow of standard gas mixture for five minutes, press the START button.
6. Close the cylinder valve.
7. As soon as the first peak, which is of hydrogen, appears on the chromatogram, list the retention time (t1) and then enter

   VALVE/EXT 1

   VALVE/EXT 2

8. The next six peaks appearing will be that of propane, isobutane, n-butane, 1-butane, trans-2-butane, cis-2-butane and pentane respectively.
9. When the last of the six peaks has appeared, list retention time (t2), and then enter

   VALVE/EXT -3

10. Wait for 0.5 minute and then enter

    VALVE/EXT -1

11. The next peak appearing will be that of methane, isobutane, n-butane, 1-butane, trans-2-butane, cis-2-butane and pentane respectively.
12. When the last of the six peaks has appeared, list retention time (t2), and then enter

    VALVE/EXT -3

13. Wait for 0.5 minute and then enter

    VALVE/EXT -1

14. The next peak appearing will be that of methane.
15. After all the methane has eluted from the column, list the retention time (t3) and enter

    VALVE/EXT 1

16. The next two peaks to appear will be that of n-hexane and i-hexane.
17. After all the i-hexane has eluted, list the retention time (t4) and then enter

    VALVE/EXT -2

18. The next two peaks to appear will be that of ethylene and ethane.
19. After all the ethane has eluted, list the retention time (t5) and then press STOP button.
20. Enter the following time programming steps:

VALVE/EXT	3
TIME	0.1
VALVE/EXT	1
TIME	t
VALVE/EXT	2

TIME	t1
FID	B
TIME	t1
ATTN 2t	9
TIME	t1+0.05
ZERO	15
TIME	t1+0.10
ZERO	15
TIME	t1+0.15
VALVE/EXT	-3
TIME	t2+0.15
VALVE/EXT	-1
TIME	t2+0.65
VALVE/EXT	1
TIME	t3+0.65
VALVE/EXT	-2
TIME	t4
STOP	
TIME	t5

21. Crack open the hydrogen and the air cylinders valves.
22. Startup the FID following manufacturer's recommended procedures.
23. Crack open the standard gas mixture cylinder again.
24. Establish a constant flow through the column.
25. Press START button.
26. Close the cylinder valve.

27. After the chromatographic analysis and the corresponding area percentage report are completed enter the following

    CALIB NORM

    RTW 5

28. Enter the retention time of each component in the standard gas mixture as shown in the chromatogram, and the corresponding volume percentage.
29. Enter

    LIST NORM

30. The response factor for each component in the standard gas mixture will be displayed.
31. The gas chromatograph is ready for sample analysis.

C.3.3 Gas Sample Run

1. Connect the product gas line to the sampling line of the gas chromatograph.
2. Establish a constant flow through the column.
3. Check and ensure the time programming steps in place are the same as that listed in Step 17 of "Calibration Run".
4. Press START button to initiate the run.
5. After the run is completed, check if any new peak is present as indicated in the chromatogram.
6. Determine the component that gives rise to the new peak.
7. Enter the retention time of any new component and the corresponding response factor.
8. Make any adjustment to the time programming, if

required, to ensure all the components elute from the column completely without being affected by the valve switching.

9. The gas chromatographic system is ready for analyzing product gas sample.
10. Press START button to initiate a sample run.
11. After the run is completed, a report listing the volume percentage of each component will be printed out.

C.3.4 Typical Daily Shutdown

1. Crack open the helium cylinder valve.
2. Close the hydrogen/helium cylinder valve.
3. Check and insure a steady flow of helium carrier gas through the columns is maintained.
4. Close the hydrogen and the air cylinders valves.
5. Turn off the TCD.

C.4 Density Measurement

The density of liquid samples may be measured with a Digital Precision densimeter, DMA 02C.

Analytical Procedure:

1. Start up the densimeter and the ultrathermostat that is filled up with water, according to manufacturer's recommended procedure.

2. Close the sample sockets with the ptfe stoppers provided.
3. Press "RESET"button and then "START" button to obtain a frequency count for air, Ta.
4. Remove the ptfe stoppers.
5. Fill the oscillator with distilled water through the lower socket with a hyperdemic syringe; ensure no air bubble is trapped.
6. Leave the hyperdemic syringe in the lower socket.
7. Close the upper socket with ptfe stopper.
8. Press "RESET" button, and then "START" button to obtain a frequency count for water, Tw.
9. Remove the ptfe stopper.
10. Withdraw the water from the oscillator by means of a hyperdemic syringe.
11. Flush the oscillator with acetone.
12. Dry the oscillator with air.
13. Fill the oscillator with the liquid sample through the lower pocket with hyperdemic syringe; again, ensure no air bubble is trapped.
14. Replace the lower ptfe stopper.
15. Press "RESET" button and then "START" button to obtain a frequency count for the liquid sample, 7s.
16. Withdraw the liquid sample with the hyperdemic syringe.
17. Flush the oscillator with acetone.
18. Dry the oscillator with air.

Calculation.

$$A = \frac{Ta^2 - Tw^2}{ds - dw}$$

$$ds = \frac{Ts^2 - Tw^2}{A} + dw$$

where T = frequency count

d = density at ultrathermostat temperature

a,w,s = air, water and liquid sample

C.5 Sulfur Content Analysis

The sulfur content of liquid samples may be measured by X-ray fluorescence. The instrument used is a Panalyzer 4000 X-ray Spectrochemical Analyzer.

Analytical Procedures:

1. Prepare and calibrate the analyzer according to manufacturer's recommended procedures.
2. Stretch a layer of Mylar film over the sample holder and retain it with a rubber band.
3. Fill the sample holder with 3 mm of liquid sample.
4. Place the sample holder over the sample orifice of the probe.
5. Close the sample cover.
6. Reset the counter to zero.
7. Set the START switch to "U" position.

8. Wait till the counter stop counting.
9. The displayed count is compared with a calibration curve to obtain the concentration of sulfur in the liquid sample.
10. The calibration curve is obtained a prior by running various samples with known sulfur content.

C.6 Determination of Hydrogen Sulfide in Product Gas

The hydrogen sulfide content of the product gas stream may be determined by iodimetric method.

Analytical Procedures:

1. Fill a gas scrubber with 50 mL of 1.0 N caustic solution.
2. Connect the scrubber to the product gas line.
3. Disconnect and remove the scrubber after the product gas stream has been allowed to bubble through the caustic solution for a reasonable time period usually 15 minutes.
4. Transfer 15 mL of the scrubbing solution to a 250 mL Erlenmeyer flash.
5. Add 10 mL of 50% sulfuric acid solution to the 15 mL of scrubbing solution.
6. Add 10 mL of 0.1 N iodine solution to the acidified scrubbing solution.

7. Titrate the solution with 0.1 N sodium thiosulphate solution to a light yellow color.
8. Add a few drops of fresh starch indicator solution.
9. Continue the titration with sodium thiosulphate solution until the end-point is reached when the solution change from blue-black to a water-white colour.

Calculation.

$$W = (Ab - An)(N)\frac{(VS)}{(Vt)}\frac{(M.W.)}{(t)} \qquad (C.5.1)$$

where W = flow rate of hydrogen sulfide, mg/min

Ab = volume of 0.1 N iodine solution used,
= 10 mL

An = volume of 0.1 N sodium thiosulphate solution used in titration, mL

N = normality of sodium thiosulphate solution used
= 0.1 N

Vs = total volume of scrubbing solution
= 50 mL

Vt = volume of scrubbing solution used in titration
= 15 mL

M.W. = molecular weight of hydrogen sulfide
= 34

t = scrubbing time, minute

APPENDIX D: LISTING OF COMPUTER PROGRAMS

```
&GCSTA T=00003 IS ON CR00135 USING 00010 BLKS R=0000
FTN4
      PROGRAM STAND
C
C     STAND PROVIDES A LINEAR CORRELATION BETWEEN RETENTION
C     TIME AND BOILING POINT FOR STANDARD MIXTURE
      DIMENSION BP(21),RT(21),D(21),D2(21),LU(5)
      DATA BP/421.,456.,488.,519.,548.,576.,602.,627.0,
     1 651.,674.696.,716.,736.,755.,774.,809.,841.,874.,
     2 928.,954.,977./
      CALL RMPAR(LU)
    5 WRITE(LU,1111)
 1111 FORMAT(/,"ENTER VALUES OF N1,N2,N3")
      READ(LU,*)N1,N2,N3
      IF(N1-99)2,999,999
    2 CONTINUE
      WRITE(LU,2222)
 2222 FORMAT(/,"ENTER VALUES OF MR,MC")
      READ(LU,* )MR,MC
      WRITE(LU,4444)
 4444 FORMAT(/,"ENTER VALUES OF RT(1) TO RT(5)")
      READ(LU,*)(RT(I),I=1,5)
      WRITE(LU,5555)
 5555 FORMAT(/,"ENTER VALUES OF RT(6) TO RT(10)")
      READ(LU,*)(RT(I),I=6,10)
      WRITE(LU,71)
 71   FORMAT(/,"ENTER VALUES OF RT(11) TO RT(15)")
      READ(LU,*)(RT(I),I=11,15)
      WRITE(LU,72)
 72   FORMAT(/,"ENTER VALUES OF RT(16) TO RT(21)")
      READ(LU,*)(RT(I),I=16,21)
  101 CONTINUE
      BP2=0.
      BP1=0.
      BPRT=0.
      RTY1=0.
      DO 11 I=1,21
      BP1=BP1+BP(I)
      BP2=BP2+BP(I)*BP(I)
      BPRT=BPRT+BP(I)*RT(I)
      RTY1=RTY1+RT(I)
 11   CONTINUE
      CC=21.*BP2-BP1*BP1
      A0=(RTY1*BP2-BP1*BPRT)/CC
      A1=(21.*BPRT-BP1*RTY1)/CC
      DO 21 I=1,21
      D(I)=RT(I)-A0-A1*BP(I)
      D2(I)=D(I)*D(I)
 21   CONTINUE
      WRITE(6,30)MR
```

```
30    FORMAT("1"," RUN NUMBER",3X,I4)
      WRITE(6,31)N1,N2,N3
31    FORMAT(" "," DATE",4X,I2," -",I2," -","  -",I2)
      WRITE(6,32)MC
32    FORMAT(" "," HP5730A NORMAL PARAFFIN CALIBRATION STD.",
     14X,I4)
      WRITE(6,33)
33    FORMAT(///," ",4X," RT",10X,"BP",9X,"D",9X,"D2")
      DO 36 I=1,21
      WRITE(6,37)RT(I),BP(I),D(I),D2(I)
37    FORMAT(" ",4F10.2)
36    CONTINUE
      WRITE(6,41)A0,A1
41    FORMAT(///," "," A0=",4X,F12.8,/,"  A1=",4X,F12.8)
      WRITE(LU,3)
3     FORMAT(//,"  MORE ? 1 - YES  2 - NO ")
      READ(LU,*)IFLAG
      IF(IFLAG.EQ.1) GO TO 5
999   STOP
      END
```

```
FTN4
      PROGRAM NEWS1
C
C     SIMULATED DISTILLATION OF LOW BOILING PETROLEUM PRODUCTS
C     (SIDLO)
C
C     SIDLO IS PRIMARILY DESIGNED TO SIMULATE DISTILLATION ON
C     GAS CHROMATOGRAPH
C
C
C     ABSTRACT
C
C          IN THE GAS CHROMATOGRAPHIC ANALYSIS OF LOW BOILING
C     PETROLEUM PRODUCTS, THE AREA UNDER THE CHROMATOGRAM IS
C     DIVIDED INTO 31 SLICES, (A(I),I=1,31), AT EQUAL INCREMENT
C     OF RETENTION TIME. THIS AREA HAS TO BE CORRECTED FOR
C     BASELINE DRIFTING. THE TRUE AREA, AL(I), IS FOUND BY
C     deducting L(I) FROM A(I), WHERE L(I) IS THE AREA SLICE
C     I UNDER THE BASELINE.
C
C          THE TRUE CUMULATIVE AREA, WAC(I), IS FOUND BY SUMMING
C     ALL SLICE AREAS UP TO AND INCLUDING SLICE I. WHEN THE
C     TOTAL CUMULATIVE AREA, AA, IS DETERMINED, THE AREA PERCENTAGE
C     OF EACH AREA SLICE, WT(I), CAN BE CALCULATED ACCORDINGLY.
C
C          ASSUMING SAME RESPONSE FACTOR FOR EACH AREA SLICE, THE
C     VOLUME PERCENTAGE BECOMES THE SAME AS THE AREA PERCENTAGE.
C     THIS IS HOW VOLUME PERCENTAGE IS DETERMINED.
C
C          THE RETENTION TIME VARIES LINEARILY WITH THE BOILING
C     POINT OF PARAFFIN. A CALIBRATION CURVE OF RETENTION TIME
C     VERSUS BOILING POINT IS OBTAINED BY A LINEAR LEAST SQUARE
C     FIT OF GAS CHROMATOGRAPHIC RESULT OF A CALIBRATION MIXTURE
C     CONTAINING N-C12 TO N-C40.  RETENTION TIME, RT(I), FOR AREA
C     SLICE I, IS CONVERTED TO BOILING POINT, BP(I), BY MEANS OF
C     THE CALIBRATION CURVE.
C
C          FINALLY, TO FACILITATE INTERPRETATION OF THE RESULTING
C     SIMULATED DISTILLATION CURVE, BOILING POINTS AT REGULAR
C     INTERVALS OF VOLUME PERCENTAGE ARE INTERPOLATED BY ASSUMING
C     LNEARITY WITHIN SMALL VOLUME PERCENTAGE INTERVAL.
C
C
C     INPUT:
C
C     GAS CHROMATOGRAM AND CALIBRATION CURVE
C
C     A0    INTERCEPT OF THE CALIBRATION CURVE (RT VERSUS BP)
C     A1    SLOPE OF THE CALIBRATION CURVE (RT VERSUS BP)
C     MA    LOW BOILING PETROLEUM PRODUCT GAS CHROMATOGRAPHIC RUN
C     MC    CALIBRATION RUN NUMBER
C     ML    BASELINE GAS CHROMATOGRAMPHIC RUN NUMBER
C     MM    AREA OF REJECTION
C     MR    RUN NUMBER
```

```
C
C
C     OUTPUT:
C
C     A(I)   AREA UNDER ACTUAL GAS CHROMATOGRAM OF LOW BOILING
C            PETROLEUM PRODUCT OF SLICE I
C     AA     TOTAL CORRECTED AREA
C     AL(I)  CORRECTED AREA CONTRIBUTED BY LOW BOILING PETROLEUM
C            PRODUCT OF SLICE I
C     BP(J)  BOILING POINT FOR THE CORRESPONDING R(I), J=31+1
C     C(I)   DESIRED BOLUME PERCENTAGE
C     L(I)   AREA UNDER BASELINE OF SLICE I
C     R(I)   RETENTION TIME FOR THE CORRESPONDING C(I)
C     WAC(I) CUMULATED VOLUME PERCENTAGE OF SLICES UP TO
C            AND INCLUDING SLICE I
C     WT(I)  VOLUME PERCENTAGE OF SLICE I AFTER BASELINE
C     CORRECTION
C
C
      REAL L(31)
      INTEGER OUNIT
      DIMENSION A(31),WT(31),WAC(31),AL(31),R(14),C(14),BP(45)
      DIMENSION LU(5),P(9),Q(3),RT(31)
      DIMENSION TRT(3),ALPHA(3),WORK(3),IW(6),COEF(9),TWAC(3)
      INTGEGER SAMPLE(20)
      DATA C/0.5,5.,10.,20.,30.,40.,50.,60.,70.,
     * 80.,90.,95.,99.5,100./
C
C     INPUT DATA
C
      CALL RMPAR(LU)
      WRITE(LU,150)
  150 FORMAT(//,"   WANT TO STAY ON THIS TERMINAL FOR INPUT AND
     *OUTPUT ?",
     * /,"   Y - 1     N - 2")
      READ(LU,*)IFLAG
      IF(IFLAG.EQ.1)GO TO 203
      LUNIT=LU
      GO TO 202
  203 IUNIT=LU
      OUNIT=LU
      GO TO 162
C
C     INPUT THROUGH TERMINAL
C
  162 WRITE(IUNIT,105)
  105 FORMAT(//,"   ENTER DATE-MONTH-YEAR OF RUN (N1,N2,N3) ")
      READ(IUNIT,*)N1,N2,N3
      WRITE(IUNIT,106)
  106 FORMAT(//,"   ENTER SAMPLE RUN NUMBER (MR). ")
      READ(IUNIT,*)MR
      WRITE(IUNIT,101)
  101 FORMAT(//,"   ENTER SAMPLE NAME.     40 CHAR. MAX.")
      READ(IUNIT,100)(SAMPLE(I),I=1,20)
```

```
100   FORMAT(20A2)
      WRITE(IUNIT,107)
107   FORMAT(//,"   ENTER HP GC RUN NUMBER FOR SAMPLE (MA).")
      READ(IUNIT,*)MA
      WRITE(IUNIT,108)
108   FORMATN//,"   ENTER HP GC RUN NUMBER FOR BASELINE (ML).")
      READ(IUNIT,*)ML
      WRITE(IUNIT,109)
109   FORMAT(//,"   ENTER AREA OF REJECTION (MM).")
      READ(IUNIT,*)MM
      WRITE(IUNIT,110)
110   FORMAT(//,"   ENTER VALUES OF L(1) TO L(5) -- 5 VALUES.")
      READ(LU,*)(L(I),I=1,5)
      WRITE(IUNIT,111)
111   FORMAT(//,"   ENTER VALUES OF L(6) TO L(10) -- 5 VALUES.")
      READ(IUNIT,*)(L(I),I=6,10)
      WRITE(IUNIT,112)
112   FORMAT(//,"   ENTER VALUES OF L(11) TO L(15) -- 5 VALUES.")
      READ(IUNIT,*)(L(I),I=11,15)
      WRITE(IUNIT,113)
113   FORMAT(//,"   ENTER VALUES OF L(16) TO L(20) -- 5 VALUES.")
      READ(IUNIT,*)(L(I),I=16,20)
      WRITE(IUNIT,114)
114   FORMAT(//,"   ENTER VALUES OF L(21) TO L(25) -- 5 VALUES.")
      READ(IUNIT,*)(L(I),I=21,25)
      WRITE(IUNIT,115)
115   FORMAT(//,"   ENTER VALUES OF L(26) to L(31) -- 6 VALUES.")
      READ(IUNIT,*)(L(I),I=25,31)
      WRITE(IUNIT,116)
116   FORMAT(//,"   ENTER VALUES OF A(1) TO A(5) -- 5 VALUES.")
      READ(IUNIT,*)(A(I),I=1,5)
      WRITE(IUNIT,117)
117   FORMAT(//,"   ENTER VALUES OF A(6) TO A(10) -- 5 VALUES.")
      READ(IUNIT,*)(A(I),I=6,10)
      WRITE(IUNIT,118)
118   FORMAT(//,"   ENTER VALUES OF A(11) TO A(15) -- 5 VALUES.")
      READ(IUNIT,*)(A(I),I=11,15)
      WRITE(IUNIT,119)
119   FORMAT(//,"   ENTER VALUES OF A(16) TO A(20) -- 5 VALUES.")
      READ(IUNIT,*)(A(I),I=16,20)
      WRITE(IUNIT,120)
120   FORMAT(//,"   ENTER VALUES OF A(21) TO A(25) -- 5 VALUES.")
      READ(IUNIT,*)(A(I),I=21,25)
      WRITE(IUNIT,121)
121   FORMAT(//,"   ENTER VALUES OF A(26) TO A(31) -- 6'VALUES.")
      READ(IUNIT,*)(A(I),I=26,31)
      WRITE(IUNIT,122)
122   FORMAT(//,"   ENTER CALIBRATION RUN NUMBER (MC).")
      READ(IUNIT,*)MC
      WRITE(IUNIT,123)
123   FORMAT(//,"   ENTER VALUES OF INTERCEPT (A0) AND",1X,
     1"SLOPE (A1) OF CALIBRATION CURVE.")
      READ(IUNIT,*)A0,A1
      GO TO 66
```

```
C
C     INPUT THROUGH CARD READER
C
 206  WRITE(LU,152)
 152  FORMAT(//,"   CHECK IF ALL THE DATA CARDS ARE IN CARD
     1READER "   AND THE READY LIGHT IS ON. ENTER 1 WHEN
     2READY.")
      READ(LU,*)ICARD
      IF(ICARD.EQ.1) GO TO 99
      WRITE(LU,154)
 154  FORMAT(//,"   NOT READY YET?  TRY AGAIN.")
      GO TO 206
  99  READ(IUNIT,*)N1,N2,N3
  25  FORMAT(3I2)
   2  READ(IUNIT,*)MR,MA,ML,MM
   1  FORMAT(4I4)
      READ(IUNIT,100)(SAMPLE(I),I=1,20)
      READ(IUNIT,*)(L(I),I=1,10)
      READ(IUNIT,*)(L(I),I=11,20)
      READ(IUNIT,*)(L(I),I=21,30)
      READ(IUNIT,*)L(31)
      READ(IUNIT,*)(A(I),I=1,10)
      READ(IUNIT,*)(A(I),I=11,20)
      READ(IUNIT,*)(A(I),I=21,30)
      READ(IUNIT,*)A(31)
   3  FORMAT(10F8.0)
      READ(IUNIT,*)MC,A0,A1
   4  FORMAT(I4,2F12.9)
      GO TO 66
C
C     INITIATION
C
  66  AA=0.
      WW=0.
      DO 21 I=1,31
      RT(I)=I-0,49
      AL(I)=0.
      WT(I)=0.
      WAC(I)=0.
  21  CONTINUE
      DO 5 I=1,31
C
C     BASELINE CORRECTION
C
      AL(I)=A(I)-L(I)
C
C     CORRECTED SLICE LESS THAN REJECTION AREA IS SET TO ZERO
C
      IF(AL(I)-MM)6,7,7
   6  AL(I)=0.
      GO TO 7
C
C     CALCULATE CUMULATED CORRECTED AREA
C
```

```
    7  AA=AA+AL(I)
    5  CONTINUE
       DO 12 I=1,31
C
C      CALCULATE VOLUME PERCENTAGE OF EACH AREA SLICE AND
C      THE CUMULATED VOLUME PERCENTAGE
C
       WT(I)=AL(I)/AA
       WT(I)=WT(I)*100
       WW=WW+WT(I)
       WAC(I)=WW
C
C      OBTAIN BOILING POINT FROM CALIBRATION CURVE
C
       BP(I)=(I-A0)/A1
   12  CONTINUE
C
C      LINEAR INTERPOLATION OF BOILING POINT AT SPECIFIED VOLUME
C      PERCENTAGE
C
       DO 74 J=1,14
C
C      CHECK IF WAC(1).GT.C(J)
C
       IF(C(J).GT.WAC(1)) GO TO 89
C
C      WAC(1).GT.C(J), LINEAR INTERPOLATION IS CARRIED OUT TO
C      OBTAIN CORRESPONDING RETENTION TIME
C
       R(J)=(0.51*C(J))/WAC(1)
       GO TO 84
  89   DO 74 I=1,30
       I1=I+1
   72  WI=(WAC(I)-C(J))*(WAC(I1)-C(J))
       IF(WI-0.)77,77,74
   77  R(J)=(C(J)-WAC(I))/(WAC(I1)-WAC(I))+I
   84  JJ=J+31
       BP(JJ)=(R(J)-A0)/A1
   74  CONTINUE
C
C      OUTPUT PRINTING
C
   75  WRITE(OUNIT,30)MR
   30  FORMAT(1H1,"SAMPLE RUN NUMBER",3X,I4)
       WRITE(OUNIT,33)(SAMPLE(I),I=1,20)
   33  FORMAT(" SAMPLE NAME",4X,20A2)
       WRITE(OUNIT,29)N1,N2,N3
   29  FORMAT(" DATE",4X,I2," -",I2," - -",I2)
       WRITE(OUNIT,31)ML,MA
   31  FORMAT(" BASELINE HP5730A RUN NUMBER",4X,I4,/,
      1" OIL HP5730A RUN NUMBER",4X,I4)
       WRITE(OUNIT,30)MC
   30  FORMAT(" HP5730A CALIBRATION STANDARD ",4X,I4)
       WRITE(OUNIT,83)MM
```

```
 83  FORMAT(" AREA OF REJECTION",4X,I4)
     WRITE(OUNIT,32)
 32  FORMAT(//////, "    RT",12X,"A",9X,"L",9X,"AL",8X,"VOL",4X,
    1"ACC.VOL.",4X,"B.P.")
     DO 34 I=1,31
     WRITE(OUNIT,35)RT(I),A(I),L(I),AL(I),WT(I),WAC(I),BP(I)
 35  FORMAT(" ",F5.2,5X,3F10.0,2F10.3,F10.2)
 34  CONTINUE
     WRITE(OUNIT,38)
 38  FORMAT(/," ",7X,"RT",6X,"VOL.PERCENT",4X,"B.P.")
     DO 40 I=1,14
     JJ=I+31
     WRITE(OUNIT,41)R(I),C(I),BP(JJ)
 41  FORMAT(1X,F10.2,4X,F10.2,1X,F10.2)
 40  CONTINUE
     LUNIT=OUNIT
     IF(OUNIT.EQ.6)LUNIT=LU
     IF(OUNIT.EQ.17.OR.OUNIT.EQ.18)LUNIT=LU
     WRITE(LUNIT,200)
200  FORMAT(//,"   ANOTHER RUN?  Y - 1  N - 2")
     READ(LUNIT,*)IFLAG
     IF(IFLAG-1)999,201,999
201  WRITE(LUNIT,102)
102  FORMAT(//,"   WANT TO CHANGE THE I/O UNIT?  Y - 1  N - 2")
     READ(LUNIT,*)IO
     IF(IO-1)888,202,888
202  WRITE(LUNIT,103)
103  FORMAT(//,"   ENTER DESIRED INPUT TERMINAL NUMBER.",/,
    1"   CARD READER - 5      TERMINAL - NN.")
     READ(LUNIT,*)NEWI
     WRITE(LUNIT,104)
104  FORMAT(//,"   ENTER DESIRED OUTPUT TERMINAL NUMBER.",/,
    1"   LINE PRINTER - 6     TERMINAL - NN.")
     READ(LUNIT,*)NEWO
     IF(NEW1.EQ.6.OR.NEW.EQ.5) GO TO 202
     IUNIT=NEWI
     OUNIT=NEWO
888  LU=LUNIT
     IF(IUNIT.EQ.5) GO TO 206
     IF(IUNIT.EQ.17.OR.IUNIT.EQ.18) GO TO 99
188  WRITE(LUNIT,221)
221  FORMAT(//,"   CHECK IF THE DESIRED TERMINAL IS READY OR NOT
    1"   ENTER 1 IF YES.")
     READ(LUNIT,*)ITERM
     IF(ITERM-1)188,163,188
163  LU=NEWI
     GO TO 162
999  STOP
     END
```

APPENDIX E: SAMPLE CALCULATION

Detailed calculation and interpretation of the experimental data were carried out in the following manner. The experiment conducted on September 25, 1979 (Run #9031) is used to illustrate the procedures involved. Raw experimental data are listed in Table F.1.

E.1 Operating Conditions

E.1.1 Reactor Temperature and Reactor Pressure

Reactor temperature was measured with thermocouple, TR-403, and recorded on Recorder 2. Reactor pressure was measured with pressure transmitter, PT-405. Agitator speed was measured with a tachometer.

Reactor temperature, $T = 450°C$

Reactor pressure, $P = 138$ MPa

Agitator speed, $A = 800$ rpm

E.1.2 Flow Rate of Feed and Product

E.1.2.1 Flow Rate of Liquid Feed and Liquid Product

The weights of liquid feed tank and liquid product tank were measured with scales. They were recorded concurrently at 10-minute intervals for two hours, after the system has reached steady state.

The depletion of liquid feed and the accumulation of liquid product were correlated with time, using a linear

least square fit. The slopes of the fitted straight lines gave the mass flow rates. The accumulation of liquid product was corrected for the samples withdrawn for analysis.

Depletion of liquid feed, $M_f = \dot{M}_f t + \text{constant}$

Accumulation of liquid product, $M_p = \dot{M}_p t + \text{constant}$

where t = time, minute

$\dot{M}_f$ $\dot{M}_p$ = Mass flow rates of liquid feed and liquid product respectively, g/min

Mass flow rate, of liquid feed $= \dot{M}_f = 0.9136$ g/min $= 0.05482$ kg/h

Mass flow rate, of liquid product $= \dot{M}_p = 0.8727$ g/min $= 0.05236$ kg/h

To convert mass flow rates into volumetric flow rates, the specific gravities of liquid feed and liquid products were used:

Volumetric flow rate of liquid feed, $\dot{F}_f = \dfrac{\dot{M}_f}{SG_f}$

$= \dfrac{(0.05482 \text{ kg/h})}{(0.9148 \text{ kg/L})}$

$= 0.05993$ L/h

Volumetric flow rate of liquid product, $\dot{F}_p = \dfrac{\dot{M}_p}{SG_p}$

$= \dfrac{(0.05236 \text{ kg/h})}{(0.8816 \text{ kg/L})}$

$= 0.05939$ L/h

where SG_f, SG_p = specific gravities of liquid feed and liquid product respectively.

E.1.2.2 Liquid Hourly Space Velocity LHSV

When the reactor is disassembled, the liquid content in it was removed by vacuum pump, and weighed. This liquid mass content was taken to be the liquid mass holdup, $LH_{w,1}$,

Liquid Mass holdup, $LH_{w,1}$ = 0.02074 kg

Assuming the specific gravities of the reactor liquid content and the liquid product to be the same, the liquid volume, $LH_{v,1}$ can be calculated as following:

$$\text{Liquid volume holdup, } LH_{v,1} = \frac{LH_{w,1}}{SG_p}$$

$$= \frac{(0.02074 \text{ kg})}{(0.8816 \text{ kg/L})}$$

$$= 0.02353 \text{ L}$$

Based on the liquid volume holdup, $LH_{v,1}$ the liquid hourly space velocity (LHSV) can be calculated.

$$LHSV = \frac{F_f}{LH_{v,1}}$$

$$= \frac{(0.05993 \text{ L/h})}{(0.02353 \text{ L})}$$

$$= 2.547 \text{ h}^{-1}$$

E.1.2.3 Flow Rate of Gas Feed and Gas Product

The cumulative volume of gas feed was measured with American dry gas test meter at 1-minute intervals for 25 minutes. The measurement was taken when the reactor system had reached reacting pressure and ambient temperature. It was correlated with time, using a linear least fit.

Accumulated flow of Gas Feed, $G_{V,f} = \dot{G}_{V,f}\, t$ + constant

where $\dot{G}_{V,f}$ = volumetric flow rate of gas feed,

t = time, h

Volumetric flow rate of gas feed = $\dot{G}_{V,1}$

= 0.0237 m^3/h

Furthermore, assuming the feed gas behaves ideally, the volumetric flow rate of feed gas at dry gas test meter pressure, P_m KPa, and ambient temperature, T_m °C, was normalized to standard conditions (101.3 KPa and 15°C)

Volumetric flow rate of feed gas at STP,

$$(\dot{G}_{V,f}) = \frac{(\dot{G}_{V,f})(P_m + P_a)(288)}{(T_m + 273)(101.3)}$$

$$= \frac{(0.0237 m^3/h)(1.72 + 94.06)MPa(288)K}{(26.5 + 273)K\ (101.3)MPa}$$

$$= 0.0216\ m^3/h$$

where P_m, T_m = operating pressure and temperature of dry test gas meter in KPa and °C respectively

P_a = Atmospheric pressure as measured with barometer KPa

By assuming the feed gas to be 100% hydrogen, the volumetric flow rate of gas feed is expressed in terms of the liquid feed as hydrogen to oil ratio, H_2/Oil,

$$H_2/\text{Oil} = \frac{(\dot{G}_{v,f})}{\dot{F}_f} = \frac{(0.0216\ m^3/h)(1000\ L/m^3)}{(0.05993\ L/h)}$$

$$= 360\ m^3/m^3$$

Similar to hydrogen feed rate, the volumetric flow rate of the product gas was obtained with American dry gas text meter, when the system had stabilized at operating conditions.

Cumulative flow of gas product, $\dot{G}_{v,p} = \dot{G}_{v,p}\ t$ + constant

Volumetric flow rate of gas product $= \dot{G}_{v,p}$

$= 0.0254\ m^3/h$

$$\text{Volumetric flow rate of gas product as STP, } (G_{v,p})_{STP} = \frac{(\dot{G}_{v,p})(P_m+94.06)(288)}{(T_m + 273)(101.3)}$$

$$= \frac{(0.0254 m^3/h)(1.72+94.06)MPa(288K)}{(26.0+273)K(101.3MPa)}$$

$$= 0.0231\ m^3/h$$

where t = time, h

P_m, T_m = measured operating pressure, KPa, and temperature, °C, respectively

The final operating conditions are summarized in Table 7.

E.2 Material Balance

Material balance of the overall system was carried out for each run. The balance was based on the average mass flow rates.

Total Feed = Total Product

$$\dot{M}_f = \dot{M}_p$$

$$\dot{M}_{l,f} + \dot{M}_{v,f} = \dot{M}_{l,p} + \dot{M}_{v,p}$$

where $\dot{M}$ = average mass flow rate gm/min

L,v = liquid and vapor respectively

f,p = feed and product respectively

Liquid feed and liquid product flow rates were found to be,

$$\dot{M}_{l,f} = \dot{M}_f$$
$$= 0.05482 \text{ kg/h}$$

$$\dot{M}_{l,p} = \dot{M}_p$$
$$= 0.05236 \text{ kg/h}$$

Mass flow rates of gas feed and gas product were calculated from the volumetric vlow rates and their respective molecular weight. In the case of gas feed, it was assumed to be 100% hydrogen and behaves ideally.

$$\dot{M}_{v,f} = \frac{(\dot{G}_{v,f})(P_m + P_a)(MW_{H2})}{(R)(T_m + 273)}$$

MWH2 = molecular weight of hydrogen.

R = gas constant

$$\dot{M}_{v,f} = \frac{(0.0237)\text{m}^3/\text{h}(1.72+94.06)\text{MPa}(2.02)\text{kg/kgmole}}{(8.3145)\text{MPam}^3/\text{K kgmole } (26.0+273)\text{K}}$$

$$= 0.00184 \text{ kg/h}$$

The mass flow rate of gas product, $\dot{M}_{v,p}$ was obtained from the refinery gas analysis,

$$\dot{M}_{v,p} = \frac{(\dot{G}_{v,p})(P_m+P_a)(MW_p)}{(R)(T_m+273)}$$

where MW_p = molecular weight of product gas stream,

$$MW_p = (X_{NH3})(MW_{NH3})+(X_{H2S})(MW_{H2S}) + (X_{H2})(MW_{H2})+\Sigma\,(X_{Ci})(MW_{Ci})$$

MW = molecular weight
X = mole fraction
NH3,H2S,H2 = ammonia, hydrogen sulfide and hydrogen
Ci = hydrocarbon with carbon number i ,i=1, 2....6

For hydrocarbons, molecular weights of n-paraffins were used.

$$(MW)_p = (0.0000)(1.703)+(0.01546)(34.08)+ (0.9173)(2.02)+(0.02593)(16.04)+ (0.01606)(30.07)+(0.01423)(44.10) +(0.01423)(44.10)+(0.00699)(5812) +(0.002097)(22.15)+(0.001152)(86.18)$$
$$= 4.56 \text{ kg/kgmole}$$

$$\dot{M}_{v,p} = \frac{(0.0254 m^3/h)(1.72+94.06)MPa(4.56)kg/kgmole}{(8.3145)MPa\ m^3/K\ kgmole\ (26.0+273)K}$$

$$= 0.00446 \text{ kg/h}$$

Therefore, the total mass feed flow rate, $\dot{M}_f$, was calculated to be

$$\dot{M}_f = \dot{M}_{l,f} + \dot{M}_{v,f}$$
$$= (0.05482 \text{ kg/h}) + (0.00184 \text{ kg/h})$$
$$= 0.05666 \text{ kg/h}$$

and the total mass product flow rate, $\dot{M}_p$, was found to be

$$\dot{M}_p = \dot{M}_{l,p} + \dot{M}_{v,p}$$

$$= (0.05236 \text{ kg/h}) + (0.00446 \text{ kg/h})$$

$$= 0.05682 \text{ kg/h}$$

The discrepancy in mass balance, ϵ_m, was defined as,

$$\epsilon_m = \frac{\dot{M}_f - \dot{M}_p}{\dot{M}_f} \times 100\%$$

$$= \frac{0.05682\text{kg/h} - 0.05666\text{kg/h}}{0.05666\text{kg/h}} \times 100\%$$

$$= 0.3\%$$

E.3 Hydrogen Consumption

Hydrogen consumption for each run was calculated from the difference between the volume flow rate of hydrogen in the gas feed and the gas product.

Hydrogen consumption, $H = (\dot{G}_{H,f})_{STP} - (\dot{G}_{H,p})_{STP}$

where $(\dot{G}_{H,f})_{STP}$ = volumetric flow rate of hydrogen in gas feed

$(\dot{G}_{H,p})_{STP}$ = volumetric flow rate of hydrogen in gas product

Since the feed gas could be assumed to be 100% hydrogen, therefore

$$(\dot{G}_{H,f})_{STP} = (\dot{G}_{v,f})_{STP}$$

$$= 0.0216 \text{ m}^3/\text{h}$$

On the other hand, volumetric flow rate of hydrogen in the product gas stream was found to be

$$(\dot{G}_{H,p})_{STP} = (X_{H_2})(\dot{G}_{v,p})_{STP}$$

$$= (0.9173)(0.0231\ m^3/h)$$

$$= 0.0212\ m^3/h$$

where X_{H_2} = mole fraction of hydrogen in product gas stream

Consequently, the hydrogen consumption was calculated to be,

$$H = (0.0216 - 0.0212)m^3/h = 0.0004\ m^3/h$$

Based on the liquid feed rate, $\dot{F}_f$, H becomes

$$H = \frac{0.0004\ m^3/h}{0.05993\ mm^3/h} = 6.7\ m^3/m^3$$

APPENDIX F: DETAILED EXPERIMENTAL DATA

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Run Number	9022	9027	9028	9029	9030	9031
Liquid Feed Rate, kg/h	0.0600	0.1055	0.0922	0.0818	0.0830	0.0548
Liquid Product Rate kg/h	0.0550	0.1005	0.0883	0.0811	0.0789	0.0524
Hydrogen Feed Rate*, m^3/h	0.0162	0.0401	0.0349	0.0355	0.0374	0.0216
Effluent Gas Rate*, m^3/h	0.0111	0.0352	0.0351	0.0525	0.0379	0.0231
Temperature, °C	449	447	448	449	450	450
Pressure, MPa	17.2	17.2	17.2	13.8	13.8	13.8
Agitator Speed, rpm	800	800	800	800	800	800
Liquid Holdup, kg	0.02680	0.03474	0.02535	0.01574	0.02449	0.02074

* Corrected to standard conditon of 15°C & 101.3 MPa

Table F.1: Data for Thermal Hydroprocessing Runs

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Run Number	9032	9033	9034	9035	9036	9037
Liquid Feed Rate, kg/h	0.0559	0.0493	0.0543	0.0578	0.0811	0.0408
Liquid Product Rate kg/h	0.0506	0.0470	0.0510	0.0554	0.0784	0.0362
Hydrogen Feed Rate*, m^3/h	0.0184	0.0178	0.0214	0.0186	0.0291	0.0201
Effluent Gas Rate*, m^3/h	0.0183	0.0388	0.0201	0.0185	0.0408	0.0102
Temperature, °C	449	451	449	450	450	452
Pressure, MPa	13.8	17.2	17.2	13.8	17.2	17.2
Agitator Speed, rpm	800	800	800	800	800	800
Liquid Holdup, kg	0.02543	0.01773	0.02251	0.02524	0.02552	0.02879

* Corrected to standard conditon of 15°C & 101.3 MPa

Table F.1(cont'd): Data for Thermal Hydroprocessing Runs

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Run Number	9038	9040	9041	9042
Liquid Feed Rate, kg/h	0.0418	0.0406	0.0414	0.0407
Liquid Product Rate kg/h	0.0332	0.0351	0.0383	0.0412
Hydrogen Feed Rate*, m^3/h	0.0164	0.0139	0.0163	0.0185
Effluent Gas Rate*, m^3/h	0.0117	0.0150	0.0154	0.0145
Temperature, °C	449	451	400	425
Pressure, MPa	17.2	17.2	17.2	17.2
Agitator Speed, rpm	800	800	800	800
Liquid Holdup, kg	0.02164	0.01886	0.05672	0.03644
Catalyst Type, Nalco	506	506	502	502
Weight of Catalyst, g	3.150	3.150	2.209	2.209

* Corrected to standard conditon of 15°C & 101.3 MPa

Table F.2: Data for Catalytic Hydroprocessing Runs